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RECEPTOR MODELS FOR AIRBORNE ORGANIC SPECIES

by

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16. ABSTRACT A study was performed that: 1) critically reviewed existing source emissions data to determine if variations in the organic composition of such emissions could be used to distinguish sources of airborne particulate matter and particulate organic matter; 2) attempted to develop receptor source apportionment models for three fractions of particulate organic matter and selected polycyclic aromatic hydrocarbons using an existing set of ambient aerosol measurements made at a site in New York City; 3) defined critical needs for the development of receptor models for airborne organic matter. The results of this study showed that it is possible to develop receptor source apportionment models for particulate organic species using the factor analysis/multiple regression modeling technique. It showed that a lack of adequate organic composition data for source emissions was a critical limitation for model validation and also for development of chemical mass balance receptor source apportionment models. It also showed, however, that existing source emissions data on polycyclic aromatic hydrocarbons and certain other species indicate that such species might be useful in distinguishing emissions from certain types of sources.		
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ABSTRACT

The purposes of this study were: 1) to critically review existing source emissions data to determine if variations in the organic composition of such emissions can be used to distinguish sources of airborne particulate matter and particulate organic matter; 2) to attempt to develop receptor source apportionment models for three fractions of particulate organic matter and selected polycyclic aromatic hydrocarbons using an existing set of ambient aerosol measurements made at a site in New York City; 3) to define critical needs for the development of receptor models for airborne organic matter.

The results of this study have shown that it is possible to develop receptor source apportionment models for particulate organic species using the factor analysis/multiple regression modeling technique. The lack of adequate organic composition data for source emissions was found to be a critical limitation for model validation and also for development of chemical mass balance receptor source apportionment models. However, existing source emissions data on polycyclic aromatic hydrocarbons and certain other species indicate that such species might be useful in distinguishing emissions from certain types of sources.

The most critical need for further development of such models is organic composition data for major sources of emissions. It is recommended that 1) a source emission sampler, suitable for collecting particulate and vapor phase organics, at near ambient temperature and dilutions, be developed and field tested; 2) a limited field study be conducted to confirm that differences in organic composition can be used to help distinguish emissions from different sources and 3) that more extensive source emissions data be collected to simultaneously define the organic and inorganic composition of important sources of toxic air pollutants.

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SECTION 1

INTRODUCTION

1.1 BACKGROUND

Over the past decade, there has been increasing interest in and development of receptor source-apportionment models to assist in defining control strategies for particulate pollutants. Such models attempt to identify the principal sources of airborne particles and to determine their contributions to ambient aerosol mass concentrations using measurements made at sampling, i.e., "receptor" sites. Most of the work in this field has focused on particle mass and elemental composition and this work has been reviewed by a number of authors (1-6). Very little work has been done to date on receptor models for particulate organic matter (7-11).

The organic fraction of the aerosol constitutes 10 to 40% of the airborne particles which can penetrate into the human respiratory system (12, 13). Extractable organics and many of the subfractions and compounds within the extractable organic fraction have been shown to be biologically active in both mammalian and bacterial bioassays (14-17). Thus, there is reason to suspect that the organic fraction may be of significance to human health and that control of the sources of these materials may be required.

The ultimate source of much of the primary and secondary particulate organic matter in urban and suburban aerosols is combustion of fuels for transportation, heating, power production and industrial processes. Recent trends toward increased utilization of diesel engines in light-duty trucks and autos, and of coal and wood as fuels for home heating are of particular

concern since the emissions of these sources are rich in organic compounds (18, 19) and can impact on large population centers with severe impacts in specific neighborhoods. At present we lack the tools which would enable us to determine the amounts and classes of organic compounds (as they exist in the atmosphere) contributed by various types of sources to urban atmospheres.

Receptor source apportionment modeling techniques for particulate organic matter can be useful in several ways: 1) receptor models for determining the principal source of airborne organic pollutants, such as polycyclic aromatic hydrocarbons, would be useful in developing appropriate control strategies, should they become necessary; 2) unique organic tracers or characteristic organic composition profiles in emission sources may be useful for distinguishing sources of airborne particles which cannot be readily resolved through elemental composition profiles (e.g., soil and coal fly ash) or for identifying emissions from motor vehicles after elimination of leaded gasoline; and 3) finally, it may be possible to gain information on physical and chemical transformations of organics occurring between the source and the receptor site through such techniques.

1.2 OBJECTIVES

The purpose of this study was to investigate the potential for using receptor modeling techniques as tools for determining sources of airborne organic compounds or of particle mass. Specific objectives were:

1. To critically review the literature for organic source emission data which might be applicable for receptor models.

2. To apply several receptor modeling techniques and compare the results for an existing set of New York City ambient measurements of respirable ($D_{50} = 3.5 \mu m$) particulate organic matter.
3. To analyze samples of Philadelphia particulate matter for organic species and, if possible, use these data for further development of receptor models.
4. To evaluate the results of objectives 1 through 3 in order to define critical needs in the development of receptor models for airborne organic matter.

Specific questions addressed in this review were:

1. Do the literature data show significant differences in source emission patterns of particulate organic compounds which may be useful in developing "fingerprints" for receptor source apportionment models? If so, for which classes of compounds and what source types?
2. Are there any organic or carbon species that could be used as unique source tracers?
3. Can existing source emissions data be used to develop organic receptor models or to distinguish sources of airborne particle mass or will additional data be required?
4. If additional data are required, which classes of compounds or organic fractions should be the focus of first efforts in development of receptor models?

SECTION 2

EXECUTIVE SUMMARY AND CONCLUSIONS

2.1 PURPOSE OF STUDY

The purpose of this study was three fold: 1) to review existing data and to determine if these data indicate that variations in the organic composition of source emissions could be used to distinguish sources of airborne particulate matter and particulate organic matter; 2) to determine if receptor modeling techniques could be used to identify the sources of airborne particulate organic pollutants and to estimate their contributions; 3) to define critical needs in the development of receptor source apportionment models for particulate organic species.

2.2 CRITICAL REVIEW OF EXISTING PARTICULATE ORGANIC SOURCE EMISSIONS DATA

Available literature on the organic composition of emissions from major sources of organic particulate pollutants were critically reviewed to determine if the existing data show significant differences among sources which would be useful in developing "fingerprints" for receptor source apportionment models? If so, for which classes of compounds and what source types? Data were also sought on unique organic or carbon species that could be used as source tracers. The adequacy of the existing data for receptor modeling was then evaluated.

Based on existing emissions inventories, emphasis was placed on obtaining particulate organic source emission data for motor vehicles, home heating (gas, oil, wood and coal), industrial boilers, power plants (oil, coal, gas), large incinerators, coke production, petroleum refining and soil.

The classes of organic compounds selected for the literature search were those known to be present in the ambient aerosol or in source emissions which might be useful in distinguishing sources of particulate matter. These were polycyclic aromatic hydrocarbons (PAH), aliphatic hydrocarbons, carboxylic acids, aza-arenes (nitrogen heterocyclics), sulfur heterocyclic PAH and nitro-PAH.

Copies of approximately 180 publications were obtained and reviewed. Relatively few of these reported data which were suitable for the purpose of this review. As expected, the majority of those which were suitable, reported PAH measurements. For each source sample, the ratios of individual PAH compounds to a reference compound, benzo(e)pyrene, were calculated and these data were compiled for comparisons among sources. Major factors to be considered in comparing the existing organic source composition data were reviewed and discussed. These include the effects of combustion conditions, sampling protocols, sample preservation, extraction and analytical methods on the reported PAH or other organic compound profiles.

Despite their many limitations, the existing data were judged to provide some useful information with respect to receptor modeling. First, the PAH profiles of sources which have been repeatedly sampled and analyzed by the same investigators appear to be quite reproducible. Secondly, the existing data indicate that there are organic compositional differences which can be exploited for differentiating certain sources. Furthermore, the data provide indications of which compounds should be investigated more fully. The PAH compounds in particular, appear most promising. Their proportions in

emissions (gas plus particle) from a given source type frequently vary over several orders of magnitude which enhances their potential usefulness for source discrimination. There also appear to be several unique or almost unique PAH tracers which may be useful. The existing data provide a basis for selecting those compounds within this class which are likely to be most stable in the atmosphere. In addition, good sampling and analytical methods already exist for this class of compounds.

There are, however, many deficiencies in the existing data on the organic composition of source emissions. These data have generally been collected for the purpose of determining emission rates and are consequently inadequate for use in receptor source apportionment modeling. The principal reasons for this are:

1. Data generally exist only for the PAH compounds and even these have not been adequately measured in many sources of interest. Other composition variables, e.g., other classes of organics, trace elements, carbon and particle mass have rarely been measured simultaneously for the same source.
2. Existing organic composition data are rarely representative of the average emissions for a source type. Usually, they represent a single source and a single set of operating conditions for that source.
3. Sampling methods used for source emissions are frequently incompatible with those used for ambient samples collected at a receptor site. In the case of source sampling, organic vapors are

frequently collected separately from emitted particles. For ambient samples, organic vapors are rarely collected with the particles. In addition, sampling duration (and filter loading) differ for the two types of samples which may also affect composition.

4. Differences in the particle size cuts of collected samples affect composition.
5. The analytical methods and quality assurance practices used to collect existing source composition data vary widely. For receptor modeling, both accuracy and precision of the measurement are critical.

Finally, it should be recognized that changes in the composition of source emissions can occur as a consequence of regulation and technology; consequently receptor and source sampling and analysis methods and measurements must continuously be updated for receptor modeling.

2.3 DEVELOPMENT OF RECEPTOR SOURCE APPORTIONMENT MODELS FOR PARTICULATE ORGANIC MATTER

In order to evaluate the feasibility of developing receptor source apportionment models for particulate organic matter, an existing set of ambient aerosol measurements was analyzed using the factor analysis - multiple regression modeling method that had been developed previously in this laboratory by Kleinman et al. (2). This modeling method was selected because the lack of adequate organic source emissions composition data precluded the development of chemical mass balance models.

Weekly samples of respirable ($D_{50} = 3.5 \mu m$) particulate matter which had been collected on the roof of a 15 story building in the Manhattan section of New York City during 1979 and 1980 had been analyzed for three fractions of extractable organic matter (EOM), polycyclic aromatic hydrocarbons, several trace elements (V, Pb, Cu, Mn) and water-soluble sulfate. This data base was extended by XRF analyses for additional trace elements (Fe, Mo, P, Br, Ti and Ni) and a second analysis (XRF) for Pb, V and S. The concentrations of three organic fractions of increasing polarity were determined by sequentially extracting the particulate samples with cyclonexane (CX), dichloromethane (DCM) and acetone (ACE).

Factor analysis was used to identify major sources of airborne particulate organic matter. Six to nine factors were obtained, depending upon the number of variables included in the factor analysis. A consistent pattern of factors was observed with the following major sources being identified through the high factor loadings for certain source tracer elements: 1) oil-burning (V); 2) motor vehicles (Pb, Br); 3) resuspended soil (Fe, Ti, Mn); 4) sulfate-related aerosol (SO_4^{2-} , S); 5) incineration (Cu). These factors were consistent with the known sources of airborne particulate matter in New York City, where residual oil is the major fuel used for power generation and space heating. Neither wood nor coal are currently used as fuels.

Multiple regression models of the form:

$$[\text{Organic fraction}] = k_1 T_1 + k_2 T_2 + \dots + k_i T_i + R$$

were developed, where the T_i are concentrations of source tracer elements selected from the factor analysis, the k_i are multiple regression coefficients

and R is the portion of the concentration of organic matter which cannot be attributed to any of the sources of the model. The coefficients, which are determined from the ambient measurements, are proportional to the ratios of particulate organic matter to tracer elements in the source emissions. Consequently, these coefficients were compared to available source emission data for model verification. The multiple regression models were then used to estimate the average contributions of various source types to each organic fraction.

The models indicated that residual oil burning and resuspended soil were the major sources of respirable particulate organics at this site during 1979 and 1980. These two sources accounted for $24 \pm 4\%$ and $21 \pm 8\%$ of the total EOM (CX + DCM + ACE), respectively. Sulfate-related organic aerosol accounted for an additional $15 \pm 6\%$ of EOM while motor vehicles and incineration each contributed 6% at this rooftop site in Manhattan.

The models indicate that the sources of organic aerosol can be different for fractions of differing chemical composition. For example, sulfate-related organic aerosol was found only for the more polar DCM and ACE fractions which would contain any secondary organic aerosol.

Twenty-nine percent of the total EOM could not be attributed to known sources but is suspected to originate, in part, from upwind urban and regional background sources. Unidentified sources may contribute to the residual, as well. The possible influence of filter sampling artifacts on the residual must also be considered. The samples used for model development were collected over periods of one week in order to maintain continuity with TSP

sampling begun in 1967. For organic sampling, 12 or 24 hr. samples would be more appropriate as volatilization losses and filter reactions would be minimized.

Seasonal variations in temperature and aerosol surface area can affect the distribution of organics between the vapor and particulate phases and thus might account for some of the residual of the model for CX. A first order approximation was used to correct for such effects and account for some of the residual. The results indicated that only 3-4% of the residual could be explained in this way.

The coefficients of the model for the cyclohexane-soluble organic fraction were in good agreement with the ratios of this fraction to the tracer elements in source emission samples in those instances in which source emissions data were available. For the two other organic fractions no source emission data were available for such comparisons.

Some exploratory work has been done on developing similar source apportionment models for individual polycyclic aromatic hydrocarbons. Using a limited set of data, statistically significant models were developed for benzo(a)pyrene and for chrysene. The coefficients of the models were in good agreement with the few data available for source emissions. Since the distribution of chrysene between particulate and vapor phases is strongly temperature dependent, a Langmuir model was used to determine total chrysene concentrations based on particulate concentrations, ambient temperature and the heat of sublimation of this compound. A second chrysene model was then developed for total chrysene (vapor plus particulate). Work on PAH models is

continuing with a much larger set of PAH measurements. In addition, the use of target transformation factor analysis to develop source emissions profiles for particulate organics based on ambient measurements is being investigated.

2.4 THE PHILADELPHIA STUDY

As part of the Philadelphia Model Evaluations Study of 1982, samples of inhalable ($D_{50} \leq 15 \mu m$) particulate matter were collected for organic analyses. The purpose of this work was to provide information on the concentrations of extractable organic matter and polycyclic aromatic hydrocarbons, and, if possible to use these data for further model development.

Samples were collected every 24 hrs. between 7/25 to 8/14/82 at the Fireboat Station located at the intersection of Delaware and Allegheny Streets; the Delaware River is to the east and Interstate Highway 95 is 2 blocks to the west of the site. Heavy diesel truck traffic was observed on Delaware and Allegheny.

The geometric mean concentrations of the CX, DCM and ACE fractions during this period were 2.4, 1.9 and 7.6 $\mu g/m^3$, respectively. The average concentrations for the CX and DCM fractions at this site were both 0.4 $\mu g/m^3$ higher than those observed at the N.J. ATEOS (13) site located in Camden, N.J., to the south of this site; the ACE concentration at the Philadelphia site was 1.6 $\mu g/m^3$ higher. There was evidence of weekday-weekend variations in the concentrations of CX, with minima being observed on the weekends. Some intersite (Philadelphia and Camden) correlation was apparent for all three fractions but the strongest ($r = 0.70$, $p = 0.01$) was observed for the polar

ACE fraction which contains oxidized hydrocarbons and secondary organic aerosol formed during summertime smog episodes.

The concentrations of 12 PAH compounds (fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)-, benzo(k)-, and benzo(j)fluoranthene, benzo(e)- and benzo(a)pyrene, perylene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene) were measured daily. Concentrations of individual compounds were generally less than 1 ng/m^3 . The geometric mean concentration of benzo(a)pyrene during this period was 0.13 ng/m and values ranged from 0.03 to 1.07 ng/m^3 . The average concentrations of all PAH compounds were lower on the weekends than weekdays.

Less motor vehicle traffic (diesels in particular) in this area on the weekends was hypothesized as the reason for lower concentrations of both CX-soluble organics and PAH compounds. Both PAH compounds and the CX fraction materials are directly emitted from combustion sources, i.e., they are primary aerosol species. Source apportionment modeling was not possible due to the lack of appropriate organic source emission data.

SECTION 3

RECOMMENDATIONS

The existing literature on the organic composition of source emissions, although somewhat limited, suggests that it may be possible to distinguish certain types of sources through differences in their organic composition, e.g., emissions from diesel and spark-ignition engines, resuspended soil and coal combustion, residential oil, coal and wood combustion, and motor vehicles and coke ovens. The results of the receptor source apportionment modeling work for three fractions of extractable organic matter and selected polycyclic aromatic hydrocarbons indicate that it is feasible to develop such models to estimate the contributions of various types of sources to particulate organics in the ambient atmosphere. However, it is clear from this study that further progress in these areas will require suitable organic composition data on important combustion sources. The following recommendations are made:

1. A source emissions sampler, suitable for collecting particulate organics in temperature and pressure equilibrium with vapor phase organics, and the vapor phase organics, as well, should be developed and field tested. Such a sampler must provide for cooling and dilution of source emissions to approximate that which occurs downwind of a source. Field testing would involve comparisons of such samples with those collected by the modified EPA method 5 and those collected downwind in plumes from sources.
2. In order to confirm that differences in organic source emissions exist which can be used for distinguishing sources and receptor

modeling, it is recommended that a carefully designed winter (to avoid photochemical changes) experiment be conducted using the PAH as model compounds. Ambient and source samples should be collected at a site influenced by just a few major source types, including automobiles, diesels, and oil heating. Source and ambient samples would have to be collected in such a way that the composition data would be comparable. Vapor phase and particulate PAH should be collected for all samples. The source samples must be sufficiently representative of the average conditions of each source type.

Portions of the samples or matched samples should be analyzed for trace elements and other composition variables. The best possible quality assurance practices should be used for all organic and inorganic analyses. In view of the impending loss of Pb and Br as tracers of motor vehicle emissions, extensive chemical characterization of emissions from catalyst equipped vehicles and diesel vehicles should be undertaken to try to identify individual compounds or patterns of organic compounds which might be useful as future tracers of motor vehicle emissions. Such an experiment would determine if the organic composition of source emissions and the ambient aerosol could be reconciled and which combinations of compounds and trace elements are most useful for distinguishing the sources.

3. If the experiment outlined in No. 2 is successful, more extensive source emissions testing should be undertaken to define the organic

and inorganic composition of important sources emitting toxic substances. Sampling equipment and protocols suitable for organics, such as a dilution sampler, should be used.

SECTION 4

A CRITICAL REVIEW OF PARTICULATE ORGANIC SOURCE EMISSIONS DATA IN THE LITERATURE

4.1 APPROACH TO THE LITERATURE REVIEW

Data Sources

The approach taken for the review of the literature on organic emissions from various sources was to gather literature published since 1972. In some instances, data from earlier studies of source emissions and some ambient aerosol data were also examined. Both the National Technical Information Service (NTIS) and the Chemical Abstracts data bases were searched by computer. The most current publications were obtained through the weekly Automatic Subject Citation Alert and personal contacts. Proceedings of the Battelle International Symposia on Polynuclear Aromatic Hydrocarbons (1976-1983) (20-26), the 1981 International Conference on Residential Solid Fuels (27) and the APCA Specialty Conference on Residential Wood and Coal Combustion (28) were examined. Additional publications were identified from the literature citations in the publications which were obtained from review articles (12, 29-31) and other publications (32).

Source Types

Emphasis was placed on emissions from the types of sources known or suspected to contribute most significantly to airborne concentrations of particulate organic matter in urban atmospheres.

The major anthropogenic sources of primary particulate organic and elemental carbon are combustion processes (14, 28-32). This includes combustion of fossil fuels such as coal, oil, gas and gasoline for power

generation, space heating and transportation as well as combustion of fuels such as wood and incineration. Agricultural burning and a variety of industrial processes such as petroleum refining and steel production also contribute to tropospheric concentrations of primary particulate carbon. In addition vapor phase organics emitted from combustion processes and other sources (chemical industry, solvent usage, etc.) can contribute to aerosol burdens of particulate organic matter via chemical reactions and gas-to-particle conversions.

In order to select the classes of sources which are major anthropogenic contributors to the organic fraction of the urban aerosol, available emission inventory data were examined. The data from two inventories are summarized in Table 4.1. The emission inventory for benzo(a)pyrene was prepared in 1972 by the U.S. Environmental Protection Agency (33). Cass and co-workers (34) recently completed an emission inventory for fine particle carbon in the greater Los Angeles area for 1980. Although these inventories address only primary organic emissions and the relative proportions contributed by different sources will vary from city to city, they are useful in identifying the major combustion sources likely to affect most urban airsheds.

The data in Table 4-1 suggest that for many urban areas mobile sources and space heating are important sources of particulate carbonaceous matter. The contributions from space heating will depend strongly on the type of fuel used, e.g., emissions of BaP and organics are much higher per BTU from coal and wood than from gas and oil (18, 35). Use of wood and coal for residential heating has increased in certain areas of the U.S. (35, 36) and these sources

Table 4-1. Summary of Emissions Inventory Data Available for Benzo(a)pyrene and Fine Particle ($\leq 2.5 \mu\text{m}$) Carbon Aerosol.

Stationary Sources	Emissions of BaP ^a . MT/yr	Percentage Contributions to Total Fine Carbonaceous Aerosol Emissions in Greater Los Angeles, Jan.-Feb., 1980 ^b .
Coal-burning		9
Residential furnaces	270	
Intermediate-size furnaces	6	
Steam power plants	<1	
Oil, residential through steam power type	2	
Gas, residential through steam power type	2	
Wood, home fireplaces	23	
Incineration, municipal and apartments	3	
Open burning, coal refuse	281	
Open burning, other	24	
Petroleum catalytic cracking	6	
Coke production	0.05 to 153	
Asphalt air blowing	<1	
Fugitive Combustion (Los Angeles)	-	6
Industrial Processes (Los Angeles)	-	14
<u>Mobile Sources</u>		
Gasoline-powered motor vehicles	10	25
Diesel-powered, trucks and buses	<1	13
Rubber tire degradation and brakeware	10	16
Diesels: ships, rails, off-highway, military	nd*	13
Aircraft and other	nd*	4

a. Estimated emissions of benzo(a)pyrene (BaP) in the United States, 1972, Reference 33.

b. Estimated by Cass *et al.*, 1982, Reference 34.

* nd - not determined.

are consequently likely to be significant sources in many suburban areas and small towns. In some urban areas certain industrial processes, such as a coke production and petroleum refining, can have a very substantial impact on concentrations of aerosol organics. Based upon 1972 data, coal refuse burning is a major national source of benzo(a)pyrene but an updated inventory is necessary to determine its current significance.

Natural sources, such as plants and soil, can also contribute to the organic aerosol in urban areas. There is evidence that alkanes and alcohols in plant waxes can be directly injected into the atmosphere as sub-micron particles (30). Airborne particulate organic matter can be produced by the action of waves in lakes and oceans with natural organic films consisting of n-fatty acids, alkanes, ketones and alcohols (30). Particulate organics from this type of source will be in the coarse mode of the aerosol. Resuspension of soil and dust can also contribute to airborne particulate organics. Bridges (37) estimates that about 5% of the soil on average is organic or carbonaceous. Soil-generated aerosol has been found to be enriched in carbon relative to the soil, apparently due to the presence of plant detritus of low density (38). Soil-related organic aerosol, therefore, should be concentrated in the coarse fraction of the aerosol.

Based on the inventories and the above considerations emphasis was placed on obtaining particulate organic source emission data for motor vehicles, home heating (gas, oil, wood and coal), industrial boilers, power plants (oil, coal, gas), large incinerators, coke production, petroleum refining and soil.

Organic Compound Classes

The classes of organic compounds selected for the literature search were those known to be present in the ambient aerosol or in source emissions which might be useful in distinguishing sources of particulate matter. These were polycyclic aromatic hydrocarbons (PAH), aliphatic hydrocarbons, carboxylic acids, aza-arenes (nitrogen heterocyclics), sulfur heterocyclic PAH and nitro-PAH. As expected, the majority of the available data were for the PAH compounds.

Compilation and Evaluation of Source Emissions Data

Upon completion of the literature search, copies of approximately 180 publications were obtained and reviewed. The information contained in each publication was reviewed and summarized as shown in Figures 4-1 through 4-3. Information on sampling method, organic extraction and chemical analyses was summarized for quick reference as shown in Figure 4-1. The actual measurements of a series of selected PAH compounds, including the units of measurement, and their ratios to benzo(e)pyrene (BeP) were summarized as shown in Figures 4-2 and 4-3. The compounds shown are those which were known to be most commonly measured; however, in only a few instances, were all of these compounds measured simultaneously. Available data on particle mass [total (TSP), respirable (RSP) ($d_{50} \leq 3.5 \mu\text{m}$), and fine (FP) ($d_{50} \leq 2.5 \mu\text{m}$) particulate matter], extractable organic mass (EOM), organic (OC) and elemental (EC) carbon, trace metals and sulfate were also summarized as shown in Figure 4-2. The PAH data and, in some instance, measurements of aliphatic hydrocarbons were then plotted on semi-log graph paper and the ratios to BeP

Figure 4-1. Summary Data Sheet on Organic Composition Information
Contained in Each Publication

LITERATURE SEARCH

Class(es) of Compounds _____ Source type(s) _____

Reference _____

Sample collection method _____

Dilution _____ Cooling _____

Sampling Medium _____ Sampling Interval _____

Analytical Method _____

a. Extraction Solvent _____ Sonication/Soxhlet _____

b. Separation _____

c. Final Quantitation _____

d. Internal Standard _____

e. Limit of Detection _____

f. Uncertainty _____

g. No. of Samples/Intersample variability _____

Particle size _____ Particle mass or concentration _____

Trace Elements? _____

PAH as % of Mass _____

Other Comments:

Figure 4-2. Form Used to Summarize Concentrations of Various Species
in Source Emissions

Source: _____

Reference: _____

<u>Species</u>		<u>Concentrations,</u>						<u>(units)</u>	
	1	2	3	4	5	6	7	8	
TSP									
EOM									
TOC									
OC									
EC									
Anthracene									
Phenanthrene									
Fluoranthene									
Pyrene									
Benzo(c)phenanthrene									
Benz(a)anthracene									
Cyclopenta(cd)pyrene									
Chrysene									
Benzo(b)fluoranthene									
Benzo(k)fluoranthene									
Benzo(j)fluoranthene									
Benzo(e)pyrene									
Benzo(a)pyrene									
Perylene									
Benzo(ghi)perylene									
Indeno(1,2,3-cd)pyrene									
Coronene									
Anthanthrene									
Benzo(b)naphtho(2,1-d)thiophene									
Pb									
Br									
Ba									
V									
SO ₄ =									

Figure 4-3. Form Used to Summarize Ratios to BeP

Source Type _____

Reference:

Anthracene

Phenanthrene

Fluoranthene

Pyrene

Benzo(c)phenanthrene

Benz(a)anthracene

Cyclopenta(cd)pyrene

Chrysene

Benzo(b)fluoranthene

Benzo(k)fluoranthene

Benzo(j)fluoranthene

Benzo(e)pyrene

1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0

Benzo(a)pyrene

Perylene

Benzo(ghi)perylene

Indeno(1,2,3-cd)pyrene

Coronene

Anthanthrene

Benzo(b)naphtho(2,1-d)thiophene

1. Soluble organics -
(include units)
2. Solvent
3. Particle mass (units)

were computed and compiled (Figure 4-3) for comparison. Benzo(e)pyrene was selected as the reference PAH compound. This was based upon the results of ongoing rate studies in our laboratory and in other laboratories (39, 40) as well as theoretical considerations which suggest that this compound is fairly stable, i.e., it reacts in the atmosphere at a relatively slow rate. In addition, BeP is found almost wholly in the particulate phase. Several other stable, high molecular weight PAH were considered as well, e.g., the benzofluoranthenes, but these had been measured in many fewer samples or were not resolved chromatographically.

4.2 FACTORS TO BE CONSIDERED IN EVALUATING ORGANIC SOURCE EMISSIONS DATA

In comparing the organic composition of emissions from various sources, it must be recognized that differences in sampling and analytical methods can have a very significant influence on the reported composition data. It is important to note that the purpose of most source emission sampling and analysis has been to determine an emission rate under a given set of conditions rather than to provide organic composition "fingerprints" for receptor source apportionment modeling. The major factors which can influence the organic composition of source emissions samples are discussed below.

Effects of Combustion Conditions and Sampling Duration

Samples of emissions from mobile sources, motor vehicles in particular, can be collected in a laboratory or by sampling in a tunnel. In laboratory sampling, only a single motor vehicle can be sampled at one time. The type of engine (spark ignition, diesel), the presence of a catalytic converter, the driving cycle, age of the vehicle, and hot versus cold starts are all factors

which can affect the emissions (41, 42). There is some recent evidence that the composition of volatile organic sources does not vary much with speed, load and rate of change (43). Samples collected in the laboratory, however, are not generally representative of average on road conditions for a mixture of motor vehicles. Tunnel samples provide more useful profiles for receptor source apportionment modeling as they do represent more of an average composition for motor vehicles. However, the traffic mix can vary considerably among tunnels and urban areas. Thus, it is important to match the traffic mix for the site in question with the source profile for that mix.

Similar considerations apply for stationary sources; that is, the fuel, temperature of combustion, fuel/air ratio, fuel feed rate and cycling effects will strongly influence the emissions from these sources (44). In general, samples are collected for short intervals relative to the sampling intervals used for ambient sampling and the samples do not represent an average emission profile for that type of source.

Units of Measurement

Since the purpose of most source emissions sampling is to determine a rate of emission, the measurement units of the emissions from stationary and mobile sources are not generally compatible nor readily interconverted. For mobile sources the measurements are usually reported as $\mu\text{g}/\text{km}$ while for stationary sources $\mu\text{g}/\text{BTU}$ or ng/m^3 are the most frequently encountered units. For receptor source apportionment modeling, micrograms of organic compound per gram of particle mass is the most useful unit.

Sample Collection

Particulate organic matter exists in the ambient atmosphere as a mixture of many organic compounds of different molecular weights and volatilities. Many of the compounds are distributed between the particulate and vapor phase in proportions which depend upon temperature (45, 46), particle mass (probably surface area) (47) and probably, to some extent, upon the chemical composition of the aerosol itself. When organic materials are being emitted from a combustion source, due to the elevated temperatures of the source, much more of the organic matter is in the vapor phase. Upon emission into the ambient atmosphere, these vapor phase materials cool and are condensed and adsorbed upon particles. Thus, if particles are collected at the temperatures of the stack of a furnace or of the tailpipe of a motor vehicle, the particles will be depleted of organic matter relative to their state in the ambient atmosphere.

This fact has been long recognized and source sampling systems for organic compound analyses generally incorporate equipment for cooling and collecting vapor phase organics. For mobile source sampling in a laboratory, the hot exhaust is typically diluted 4 to 20-fold with filtered air, and thereby cooled, and the particulate matter is collected on a fiberglass filter at a temperature of 50-60°C (41, 48). In some instances, the exhaust has been cooled but not diluted (49). Tunnel samples are generally collected at ambient temperatures on fiberglass filters and the motor vehicle exhaust is diluted approximately 1000-fold upon emission and thereby cooled. Since the relative proportions of organic compounds in vapor and particles vary with

temperature of collection, the profiles of compounds in laboratory samples may differ from those of ambient samples collected at different temperatures.

The degree of dilution has been shown to affect the chemical composition of the EOM (50) of diesel exhaust samples. Gorse et al. (50) recently compared the 1-nitropyrene content of diesel exhaust determined from samples collected in a tunnel to that of samples collected in laboratories. Considerably lower concentrations were found for the diesel exhaust in tunnel samples as compared to laboratory samples, suggesting that lower dilution ratios and the consequent higher concentrations of particles, organic vapors, and nitric acid led to greater formation of this compound in laboratory samples. Recent research on the sampling of diesel exhaust (51-54) has defined many of the problems associated with sampling these emissions and has often delineated solutions. Although such work has not provided the chemical characterization data required for receptor modeling, it is useful in planning future source emissions characterization work.

Samples of organic emissions from stationary sources have been collected with a number of different sampling trains. The most common ones, the modified EPA method 5 train (55, 56), the SASS (source assessment sampling system) (56) and the sampling train used by Cuffe and Gerstle (57) in the 1960's, are shown schematically in Appendix A. These trains all involve collection of particles on a hot filter followed by a gas cooling system and separate collection of organic vapors as a condensate or on an adsorbent. Although these trains efficiently collect many of the compounds found in both vapor and particle phases, the organic vapors are collected separately from

the particles. There is reason to suspect that this may affect the relative proportions of organic compounds. Organic compounds emitted from combustion sources can undergo reactions as they are adsorbed on the surfaces of particles (58, 59) or be irreversibly adsorbed (60, 61). Thus, the composition of the emissions from a combustion source, as they exist in the ambient atmosphere, may differ considerably from the composition of a sample collected at the source by conventional sampling methods.

Finally, the sampling medium may also affect the composition of an organic emissions sample. Fiberglass filters are most commonly used for source sampling but there is some evidence that PAH compounds collected on this type of filter may undergo reactions (62, 63). Because of chemical inertness, Teflon filters or Teflon-coated fiberglass filters appear to be preferable for sampling PAH compounds (62, 63) and are probably preferable for other compounds as well.

Sample Preservation

Ideally, samples of source emissions should be kept at low temperatures and/or analyzed very rapidly after collection, to minimize losses of compounds by vaporization and reaction. Samples should be protected from light during and after collection. In most of the literature on source sampling, information on sample preservation has not been provided.

Extraction of Organic Compounds

Both the organic solvent chosen for extraction of the organic matter from the particle sample and/or the adsorbent and the method of extraction can affect the composition of the extract. For example, Tomkins and co-workers

(61) have found that benzene and toluene extract benzo(a)pyrene from coal fly ash more efficiently than does dichloromethane and that the actual recovery depended upon the particular fly ash. Similar results have been reported for diesel exhaust (41) and ambient particulate matter (64). Several investigators (65, 66) have reported that ultra-sonication gives higher recoveries of PAH than does Soxhlet extraction. Losses of compounds through volatilization can also occur during solvent reduction steps. The differences in extraction methods used by different investigators for source samples can consequently be expected to affect the measured composition of those samples.

Analytical Methods

The method selected for analysis of organic compounds in source emission samples will also affect the composition profiles which are determined. The organic extracts from source samples are generally separated first into classes of compounds, e.g. PAH, by column or thin-layer chromatography or liquid-liquid extractions and then the individual compounds within the class are further separated by chromatographic techniques such as capillary or packed column gas chromatography, high performance liquid chromatography, or thin-layer chromatography (67). Compounds are detected and quantitated by a variety of methods including flame ionization detection, mass spectrometry, ultraviolet and fluorescence spectrophotometry (67).

Recoveries of individual compounds can vary depending upon the class separation method used. The reported data may or may not be corrected for recoveries. The resolution of individual compounds will vary, as well, depending upon the final separation method. Frequently the isomeric benzo(a)-

and benzo(e)pyrenes are not resolved. There can also be some ambiguity in the identification of individual compounds. Information on the accuracy and precision of the analytical method are not generally reported and frequently have not been determined.

Summary

In summary, the three most critical factors limiting the intercomparability of available organic composition source emission profiles and their use in receptor source apportionment modeling are:

1. The incompatibility of source sampling methods and sampling intervals which have been used to date with ambient aerosol sampling methods;
2. The general lack of source emission profiles which represent an average for a given type of source;
3. Differences in organic profiles due to variations among sampling and analytical methods rather than variations in source emissions.

All of these factors must be kept in mind when comparing the organic composition data currently available for source emissions. The most valid comparisons among sources will generally be for samples collected and analyzed within a given laboratory using the same sampling and analytical method for all samples.

4.3 POLYCYCLIC AROMATIC HYDROCARBONS

The PAH are, by far, the class of particulate organic compounds most frequently measured in source emissions and in the ambient aerosol. The available data on this class have been summarized in Tables 4-2 and 4-15 in a

standardized form as ratios to benzo(e)pyrene (see p. 24 for rationale) and are grouped by source type. Measurements of PAH in urban areas have also been included in these tables as they provide useful information. In comparing these data, two questions will be considered: Within the limitations due to differences in sampling and analysis -

- (1) How well do the reported profiles for a given source type agree within and among laboratories?
- (2) Are there major differences in the PAH profiles from different types of sources?

4.3.1 Interurban and Intraurban Differences

The idea of distinguishing sources of PAH through differences in their relative proportions in source emissions was first suggested in 1962 by Sawicki (68). Measurements by Hangebrauck and co-workers (69) of PAH in emissions from a large number of source types suggested that the ratios of certain compounds might be useful in distinguishing certain types of sources. In 1974, Bartle et al. (70) reported the use of high resolution glass capillary columns for separating PAH in urban particulate matter. The chromatographic profiles of samples collected at three locations in Indianapolis, Indiana, at sites influenced by emissions from industrial sources, motor vehicles and residential space heating (oil and gas) differed qualitatively from each other. No quantitative data were reported and variations in the patterns at a given site were not determined nor were analytical uncertainties examined.

More recently Grimmer and co-workers (71) have reported similar observations for samples collected in different areas of Essen, an industrial city in the Federal Republic of Germany. One-hour samples were collected once a month on fiberglass filters with a low-volume sampler in 4 areas of the city dominated by a) hand-stoked residential coal furnaces; b) oil heating; c) motor vehicle traffic (tunnel); d) coke ovens. Samples were extracted with toluene and after clean-up, the PAH fraction was analyzed by capillary column gas chromatography. The PAH profiles at the station in the coal burning area measured in January, February, March and April, 1979 were very similar although the absolute concentrations varied more than ten-fold. This was also true for motor vehicle emissions samples collected in the tunnel. Profiles measured at different times on the same day were also very similar. The PAH profiles from different areas of the city, however, showed some significant differences.

The ratios of BeP from the 4 areas are summarized in Table 4-2. As noted by Grimmer et al. (71), the relative proportion of cyclopenta(c,d)pyrene was much higher in the tunnel samples than in the samples from other areas and may be useful in recognizing this source of air pollution. Grimmer et al. (71) also noted that benzo(b)naphtho(2,1-d)thiophene was present in the air of the tunnel. Since this compound was absent in samples of automobile exhaust collected by these investigators (71), they suggested that diesel engines may be the source of this compound. Benzo(c)phenanthrene,

Table 4-2. Intraurban Variations in Ratios of PAH to Benzo(e)pyrene in Essen, FRG^a.

	<u>Tunnel</u>	<u>Residential coal-burning area</u>	<u>Residential oil-burning area</u>	<u>Coke ovens</u>
Anthracene	2.2	0.4	0.6	0.3
Phenanthrene				
Fluoranthene				
Pyrene				
Benzo(c)phenanthrene	2.2	0.4	0.6	0.3
Benz(a)anthracene	1.2	1.4	1.0	1.2
Cyclopenta(cd)pyrene	5.3	0.02	0.4	0.4
Chrysene	1.8	2.5	2.6	1.8
Benzo(b)fluoranthene	1.2	1.4	1.7	1.3
Benzo(k)fluoranthene	nr. { 1.0	nr. { 1.2	nr. { 1.5	nr. { 1.0
Benzo(j)fluoranthene				
Benzo(e)pyrene	1.0	1.0	1.0	1.0
Benzo(a)pyrene	1.2	0.6	0.9	1.0
Perylene	0.2	0.08	0.25	0.3
Benzo(ghi)perylene	1.8	0.7	1.0	0.6
Indeno(1,2,3-cd)pyrene	0.8	0.6	1.0	0.6
Coronene	0.9	0.2	0.3	0.08
Anthanthrene	0.5	0.07	0.3	0.07
Benzo(b)naphtho(2,1-d)thiophene	0.5	0.6	0.7	0.35

a. Grimmer *et al.* (1980), Reference 71.

nr. = not resolved chromatographically.

benzo(ghi)perylene and coronene appeared to be enriched in the tunnel samples as compared to those of other areas. The association of the latter two compounds with motor vehicle exhaust has been long known (68, 69). The profiles for areas influenced by coal-burning and coke production were very similar although there were differences in the proportions of cyclopenta(c,d)pyrene and perylene. This similarity may be due to the common fuel. Between oil- and coal-burning areas of this city, differences of a factor of two or more were observed in the ratios of cyclopenta(c,d)pyrene, perylene and anthanthrene. Grimmer et al. (72) have also published a detailed description of their sampling and analytical methods and the precautions that must be taken in order to obtain low backgrounds and reproducible data for profile determinations. They (72) determined that for sets of 5 analyses, the coefficient of variation for 11 PAH compounds ranged from 2.3% for benzo(e)pyrene to 9.4% for chrysene.

Lee and co-workers (73) have sampled and analyzed soot generated by combustion of coal, wood and kerosene in experimental combustors and compared the PAH compound distributions with those of ambient samples collected previously in Indianapolis and in Boston. They observed that the relative concentration of alkylated PAH from coal combustion was greater than from the other two fuels and that the coal soot contained significant amounts of sulfur heterocyclics, e.g., dibenzothiophene, benzo[def]dibenzothiophene, which were absent in the other combustion emissions. The alkyl homolog plot of the coal combustion soot was

similar to that observed for ambient particulate matter from Indianapolis, where coal is burned. Lee *et al.* (73) also noted that the concentration of high molecular weight PAH was greater for the combustion products of wood and kerosene than of coal, although the sampling and analysis methods may have affected the distribution. Although no data were reported on the reproducibility of the experimental combustors or the sampling and analytical methods, the results are indicative of composition variations which may be useful in resolving sources of PAH.

4.3.2 Motor Vehicles

The ratios of PAH to BeP for samples collected in tunnels have been summarized in Table 4-3. In most instances, the samples were collected on filters over periods of only a few hours. The samples collected in Japan in the Tsuburano and Iidabashi tunnels were collected on fiberglass filters backed by condensation traps. For these samples, the concentrations of BeP were assumed equal to those of benzo(a)pyrene, since BeP was not determined. The data have been included because the PAH profiles of spark-ignition and diesel engines were resolved from the tunnel measurements and traffic counts.

With few exceptions, the ratios agree within a factor of 5 and many agree within a factor of 3. The ratios for the more volatile pyrene and benz(a)anthracene are much higher for the Tsuburano and Iidabashi tunnels due to the use of condensation traps in the sampling train. The ratios of benzo(a)pyrene and benzo(ghi)perylene span a

larger range of values than do those of the other compounds. The ratios of these two compounds in the two Lincoln Tunnel samples (Table 4-3) appear to be unusually low (as do the absolute concentrations) compared to the 10 samples collected recently in the Caldecott Tunnel (76) and the data reported by Grimmer et al. (49) for 100 automobiles. If these two samples are omitted, the ratios of these two compounds within the remaining samples agree within a factor of 3.

Although variation over a factor of 3 may seem quite large, it must be kept in mind that the traffic mix of spark-ignition and diesel engines also varies among these tunnels. Diesels, which emit a much greater particle mass per kilometer than spark ignition engines, are only a few percent of the total for the Caldecott Tunnel but 16-24% for the Tuscarora and Allegheny Tunnels. If the ratios of trace elements to Pb are compared among samples collected in three U.S. tunnels, summarized by Pierson and Brachaczek (19), variations of this magnitude are also apparent. This is particularly true for the C/Pb ratio which ranged from an average of 1.0 (0.3-2.3) in the Caldecott Tunnel (1975-1977) to 14 for the Allegheny and Tuscarora Tunnels (1975-1979). Here again, the traffic mix has a strong influence on the aerosol composition.

Table 4-4 summarizes the available data for samples of exhaust from spark ignition engines. The samples collected by Grimmer and co-workers (49, 79), in the first 3 columns of the table, were collected by cooling the exhaust and extracting the condensate on the surface of the

Table 4-3. Ratios of PAH to Benzo(e)pyrene for Samples Collected in Tunnels^a.

Tunnel: Reference: Sample No.:	Baltimore Harbor ^b			Lincoln ^b			Holland			Caldecott	Tsuburano ^d			Iidabashi		in FRG
	74	75			1	4	6	7	8	76	Spark- Ignition ^d	77	77	78	71	
										Range for 10 samples			Diesel Engine ^d			
Anthracene																
Phenanthrene																
Fluoranthene																
Pyrene	1.4									1.0-2.0	10	42		8.8		
Benzo(c)phenanthrene	1.7									0.6-1.7						
Benz(a)anthracene																2.2
Cyclopenta(cd)pyrene	1.5	0.6	1.3	0.9	0.6	-					2.5	3.6		2.7		1.2
Chrysene																5.3
Benzo(b)fluoranthene	1.5										2.7	5.4		2.3		1.8
Benzo(k)fluoranthene										2.9-5.5						
Benzo(j)fluoranthene										0.6-1.0						
Benzo(e)pyrene	1.0	0.2	0.5	0.5	0.4	0.9				0.3-0.4						
Benzo(a)pyrene	1.0	1.0	1.0	1.0	1.0	1.0				1.0-1.4						
Perylene		0.2	0.4	0.7	-	0.8				1.0	1.0 ^e	1.0 ^e		1.0 ^e		1.0
Benzo(ghi)perylene										0.8-2.0	1.0	1.0		1.0		1.2
Indeno(1,2,3-cd)pyrene	1.2	0.4	1.4	2.6	0.9	1.2				0.2-0.7	0.28	0.34		0.3		0.2
Coronene		0.3	0.6	1.2	0.4	1.3				2.0-3.0	2.9	1.3		2.2		1.8
Anthanthrene		0.3	0.6	-	0.4	1.1				0.7-1.5						0.8
Benzo(b)naphthol(2,1-d)thiophene																0.9
																0.5
																0.5

Extraction solvent:

	benzene	cyclohexane			cyclohexane	benzene-methanol (3:1)	benzene- methanol (3:1)	toluene
Con. of particles, $\mu\text{g}/\text{m}^3$	180	137	114	197	-	161		
Con. of EOM, $\mu\text{g}/\text{m}^3$	15.5	-	-	-	-	-	c.	
Con. of Pb, $\mu\text{g}/\text{m}^3$	-	9.5	7.9	13.7	-	11.2	29.0-92.8	

a. Samples collected on filters except as noted.

b. Average of 4 samples collected on fiberglass filter with polyurethane back up.

c. Not available during preparation of this report.

d. Tokyo, Japan; contributions of spark-ignition and diesel engines determined mathematically from tunnel samples and traffic counts.

e. Concentration of benzo(e)pyrene assumed equal to benzo(a)pyrene.

Table 4-4. Ratios of PAH to Benzo(e)pyrene for Samples of Exhaust from Automobiles with Spark Ignition Engines.

No. of Vehicles:	100	1	1	1	1	26	e.
Reference:	49 ^a .	79	79	42 ^b .	42 ^c .	78 ^d .	80
Anthracene	6.9	9	17				
Phenanthrene	29	50	64				
Fluoranthene	14	18	45	2.2	0.23		11.7
Pyrene	18	36	78	3.6	0.67	13.4	19.7
Benzo(c)phenanthrene	-	-	-				
Benz(a)anthracene	-	1.4	1.4	1.1	0.2	2.9	
Cyclopenta(cd)pyrene	-	17	20	0.8	0.2		
Chrysene	4.9	2.1	2.3	1.2	0.7	3.1	
Benzo(b)fluoranthene	-	0.8	0.5				
Benzo(k)fluoranthene	-	0.3	0.2				
Benzo(j)fluoranthene	-	0.5	0.3				
Benzo(e)pyrene	1.0	1.0	1.0	1.0	1.0	1.0 ^d .	1.0
Benzo(a)pyrene	1.0	1.4	1.4	0.3	0.3	1.0	1.2
Perylene	-	0.2	0.2			0.3	0.2
Benzo(ghi)perylene	3.4	5.6	3.1	0.7	2.3	2.9	4.2
Indeno(1,2,3-cd)pyrene	0.7	1.5	0.9	0.2	1.0		
Coronene	2.0	4.6	2.9	0.3	2.7		2.8
Anthanthrene	0.7	0.3	0.7				
Benzo(b)naphtho(2,1-d)thiophene	-						
Extraction Solvent	f.	f.	f.	g.	g.	h.	g.

a. Based on Figure 3 in Reference No. 49.

b. Spark-ignition engine, average of 3 tests

c. Catalyst-equipped car, average of 3 tests.

d. Average of 26 Japanese motor vehicles; concentration of benzo(e)pyrene assumed equal to benzo(a)pyrene.

e. Data taken from Table 5 of Reference No. 80, results of round robin analyses of exhaust condensate, n = 27 to 35 analyses.

f. Cyclohexane/dimethylformamide.

g. Extraction solvent not reported.

h. Benzene-methanol (3:1).

condenser and the particles on the filter behind the condenser. Thus, the ratios of the more volatile compounds, phenanthrene, anthracene and pyrene, are relatively high for these samples. Experimental details on sample collection and analysis were not reported for the samples in columns 4 and 5. The average ratios for exhaust from 26 Japanese motor vehicles, reported by Handa *et al.* (78), shown in column 6, were from samples collected on filters backed by condensation traps in liquid nitrogen; here again, since the concentration of BeP was not determined it was assumed equal to benzo(a)pyrene; based on the other measurements, this is a reasonable assumption. The last column of the table presents the ratios of the average concentrations determined for one sample of exhaust condensate in a round robin analysis.

If the data reported by Stenberg (42) are excluded from the comparison, then the ratios of the PAH/BeP for the exhaust condensates, for compounds beyond pyrene agree within a factor of 2.3 or less, despite differences in sampling and analytical methods. Furthermore, the ratios for the exhaust condensates generally agree well with those determined for the tunnel samples. The exhaust condensates are relatively enriched in fluoranthene, pyrene, benzo(ghi)perylene and coronene. The tunnel samples also showed higher ratios of benzo(ghi)perylene and coronene (compared to compounds of similar molecular weight) although they are somewhat lower than those of the

exhaust samples. The cyclopenta(c,d)pyrene ratios for the two auto exhaust samples were also high but determinations of this compound have been limited.

The available data for diesel engines have been summarized in Table 4-5. Despite the intensive research on the mutagenic and carcinogenic activity of diesel exhaust over the past few years, there have been few reports of multi-PAH composition. Most of the papers which reported composition data, reported only the concentrations of only one or two compounds, typically benzo(a)pyrene (83-85) or nitro-PAH or have reported qualitative rather than quantitative data (86, 87). In some instances, BeP was not resolved from BaP although many individual compounds were measured (88).

The ratios in Table 4-5 are so limited that comparisons are difficult. Based on these data, it is not possible to make any judgements as to the possibilities for distinguishing diesel emissions from those of spark-ignition engines. Recently, based on measurements made in the Caldecott Tunnel, Hering *et al.* (89) have suggested that ratios of benzo(k)- and benzo(b)fluoranthene to CO may be useful in distinguishing diesels, since these ratios increase with an increase in diesel traffic. The compound benzo(b)naphtho(2,1-d)thiophene or other thiophenes may also provide a means for resolving the contributions of diesel and spark-ignition engines; thiophene compounds have been identified in tunnel samples (71) and in diesel exhaust (86).

Table 4-5. Ratios of PAH to Benzo(e)pyrene for Diesel Exhaust

Reference:	81	82 ^{a.}	77 ^{b.}
Anthracene			
Phenanthrene	1602		
Fluoranthene	63		
Pyrene	87		42
Benzo(c)phenanthrene			
Benz(a)anthracene	8.8	5 -25	3.6
Cyclopenta(cd)pyrene			
Chrysene	1.2		5.4
Benzo(b)fluoranthene			
Benzo(k)fluoranthene			
Benzo(j)fluoranthene			
Benzo(e)pyrene	1.0	1.0	1.0 ^{a.}
Benzo(a)pyrene	5.5	1.5-10	1.0
Perylene			0.3
Benzo(ghi)perylene	1.8	0.5- 1.2	1.3
Indeno(1.2.3-cd)pyrene			
Coronene			
Anthanthrene			
Benzo(b)naphtho(2,1-d)thiophene			

- a. Only samples collected at dilution ratios of 4 or greater are included.
- b. Based on tunnel measurements in Japan; the concentration of BeP was assumed equal to that of benzo(a)pyrene.

Some data on the percentages of a number of organic and inorganic components of motor vehicle emissions have been compiled in Tables 4-6 and 4-7 for comparative purposes. For the tunnel samples, benzo(a)pyrene ranged from 0.008 to 0.037% of the total particle mass (Table 4-6). Lead was consistently 7% of the particle mass for the Lincoln and Holland Tunnels' samples but only 1.6% of particle mass for the Allegheny Tunnel. These differences are probably due to the relatively high volume of diesel traffic in the Allegheny Tunnel as compared to the two N.Y.-N.J. tunnels. (It should be noted that for the Lincoln Tunnel, much of the diesel traffic passes through a separate tunnel.) In Table 4-7, the composition of diesel and gasoline engine exhaust have been determined from samples collected in the Allegheny Tunnel combined with traffic counts (19, 90). Diesel exhaust is largely carbonaceous, with a ratio of elemental or organic carbon (EC/OC) of 2.5. The percentage of EOM is almost equivalent to that of OC; this is due to the large proportion of aliphatic hydrocarbons in the EOM. The data for the gasoline engines have very large uncertainties due to the large uncertainty in the estimated particle mass emission rate. This is probably a consequence of the overwhelming influence of diesel exhaust in these samples, i.e., the mg of particles per km for the diesel engines is two orders of magnitude greater than for the spark-ignition engines and diesel traffic was 23% of the total for these samples.

It should be noted that there are many gaps in the data which have been compiled in Tables 4-3 to 4-7 and that a fairly complete set of composition data (organic and inorganic) simply does not exist.

Table 4-6. Components of Motor Vehicle Exhaust as a Percentage of Particle Mass Based on Tunnel Samples

Component	Lincoln Tunnel ^a		Holland Tunnel ^a		Baltimore Harbor Tunnel ^b	Allegheny Tunnel ^c
EOM					8.6 (benzene)	27.1 (DCM)
OC						22.7 (DCM)
EC						
BaP	0.008	0.013	0.026	0.025	0.037	
Pb	7.0	7.0	7.0	7.0		1.6
SO ₄ ⁼						2.3 ^d
Br						0.5
Ba						0.2
TSP, $\mu\text{g}/\text{m}^3$	136.5	113.5	196.8	160.9	180	231

a. 1981, samples 1, 4, 6 and 8, Reference 75.

b. 1975, Reference 74.

c. 1979 experiments; traffic mix - 76-77% gasoline powered engines, 23-24% diesel (1.8% light-duty); DCM = dichloromethane; Reference 19.

d. Particles less than 0.43 μm only.

Table 4-7. Components of Diesel and Gasoline Engine Exhaust as a Percentage of Total Particle Mass^a.

Component	Diesel Engines		Gasoline Engines	
	1979 ^a .	1981 ^b .	1979 ^a .	1981 ^b .
EOM ^c .	22.9 ± 4.4 ^c .	23.8± 4.3 ^d .	100±120 ^c .	33± 51 ^d .
Pb	0.3 ± 0.1		65± 66	
SO ₄ ⁼	2.9 ± 0.5			
Br	<0		33± 33	
Ba	0.14± 0.04			
Total Carbon		76.2±13.5		67±127
Elemental C		54.8± 9.2		67±103
Organic C		21.4± 5.3		17± 55
TSP, mg/km	860±22	840±90	6±6	6±7

a. Based on sampled collected in the Allegheny Tunnel, Reference 19.

b. Based on samples collected in the Allegheny Tunnel, Reference 90.

c. Extracted with dichloromethane followed by acetonitrile.

d. Extracted with 1:1 toluene and n-propanol.

4.3.3 Oil- and Gas-Fired Residential Furnaces

Oil- and gas-fired furnaces provide residential heating in the majority of U.S. homes. On an annual nationwide basis, emissions from these units have been estimated to contribute less than 1% of the BaP emissions (33). Although the emissions per unit are low for these types of sources, the use of these units is heavily concentrated in the northeastern U.S. which burns about 60% of all residential heating oil (91). In many areas of the northeast with a high density of housing, under wintertime meteorological conditions, emissions from such units can make a substantial contribution to ambient concentrations of TSP and EOM.

Recent measurements in a residential area of Elizabeth, N.J., where gas and oil are used for heating, indicate the potential impact of these emissions (13). During a winter sampling period during the peak of the space heating season, the average concentration of EOM over a six week period was almost twice the summer average although the average concentration of inhalable particulate matter was only one-third higher in winter compared to summer. The extractable organic fraction constituted 33% of the inhalable particle mass as compared to 22% during the summer (13).

Despite their potential significance there have been few measurements of emissions from these types of sources. Cha and co-workers (91) recently sampled emissions from two new design oil-fired heating units of high efficiency and determined the concentrations of

dichloromethane (DCM)-soluble organics but did not analyze the samples for PAH. Castaldini *et al.* (92) sampled and analyzed emissions from an oil-fired, low emission, residential heating unit under continuous and cyclical operating conditions. Samples were collected with a SASS train and extracted with dichloromethane. Organic emissions (DCM-soluble) were 20-times greater (26.3 vs. 1.3 mg/m³) under cyclical than continuous operation. Infrared spectra indicated that most of the organic mass was aliphatic hydrocarbons. Only a few PAH compounds could be quantitated in the collected samples. Phenanthrene/anthracene, pyrene and fluoranthene were present at concentrations of 767, 9 and 26 ng/m³, respectively. It should be noted that this unit is not typical of those currently in use in most homes.

The only other available data on PAH in emissions from residential oil and gas furnaces are from samples collected in the 1960's (69). These data are presented in Table 4-8 in units of μg per 10^6 BTU. Ratios to BeP could not be calculated since this compound was not measured. For the oil-burners, although the data are limited to 3 samples, fluoranthene appears to be enriched relative to pyrene. The data reported by Castaldini *et al.* (92) also suggests a higher proportion of fluoranthene than pyrene. These two compounds were present in tunnel samples and motor vehicle exhausts in approximately equal amounts (Tables 4-3 to 4-5), suggesting that it may be possible to distinguish between emissions from oil-burners and motor vehicles. This

would have to be confirmed, however, since the number of samples is so very limited.

Polycyclic aromatic hydrocarbon measurements are available for only two gas-fired units (Table 4-8). Hangebrauck et al. (69) noted that for two gas-fired furnaces (not residential furnaces), the ratios of benzo(a)pyrene to benzo(ghi)perylene and coronene were similar to those observed for automobile exhaust. For three of five gas-fired units (residential and institutional), pyrene was the only compound of consequence (69).

4.3.4 Coal-Fired Residential Furnaces

As the prices of oil, gas and wood have increased, the use of coal for residential space heating has also increased, particularly in the northeastern U.S. (27, 28). As first demonstrated by the classical work of Hangebrauck, von Lehmden and Meeker (69), emission of benzo(a)pyrene and other PAH per BTU gross heat input are much greater for combustion of coal than for oil or gas. In addition emissions of PAH are much greater for residential coal-burning furnaces than for large, efficient furnaces operated at high temperatures with a sufficient excess of air.

The ratios of PAH to BeP from recent measurements of emissions from coal-burning stoves, reported by Sanborn et al. (93) are presented in Table 4-9. The samples were collected with a modified EPA method 5 train and then extracted with dichloromethane. The filter was re-extracted with toluene and the combined extracts were fractionated by

Table 4-8. Emissions of PAH from Residential Oil- and Gas-Fired Burners^a.

Sample No.	$\mu\text{g per } 10^6 \text{ BTU heat input}$				
	Residential Oil-Burners			Residential Gas-Burners	
	13	15	17	16	18
Phenanthrene			8,900	77	
Pyrene	15	1,200	1,800	120	170
Fluoranthene	76	15,000	5,000	110	320
Benzo(a)pyrene	<60	<100	<40	<20	<20
Benzo(e)pyrene				18	

a. Hangebrauck et al. (1967); Reference 69.

Table 4-9. Ratios of PAH to Benzo(e)pyrene in Emissions for Residential Coal Burning^a.

Coal Type: Burn Rate:	Anthracite ^{a.,b.}		Bituminous ^{a.,b.}		Anthracite ^{a.,b.} "Wood" Stove ^{c.}	Bituminous ^{a.,b.} Moderate Rate	Bituminous ^{d.}
	High	Low	High	Low			
Anthracene	7.5	2	2.1	2.6	3	1.9	5.1
Phenanthrene	69	20	7.2	4.7	30	3.9	20
Fluoranthene	54	21	3.6	2.0	16	3.2	7.1
Pyrene	39	12	2.1	1.8	12	2.2	5.5
Benzo(c)phenanthrene							
Benz(a)anthracene	34	3.0	1.3	1.2	3.7	2.0	2.5
Cyclopenta(cd)pyrene							
Chrysene	37	5.0	1.5	1.0	5.0	1.6	1.8
Benzo(b)fluoranthene							
Benzo(k)fluoranthene	4.3	3.0	1.9	2.4	4.3	3.3	
Benzo(j)fluoranthene							
Benzo(e)pyrene	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Benzo(a)pyrene	0.6	2.0	1.1	1.4	0.6	1.4	0.6
Perylene	0.1	0.5	0.1	0.1	0.1	0.2	2.1
Benzo(ghi)perylene	1.9	1.0	0.5	0.6	0.3	0.8	
Indeno(1,2,3-cd)pyrene	2.3	1.0	0.1	1.0	0.6	1.8	
Coronene	1.3	0.25	0.6	0.2	0.4	0.5	
Anthanthrene	0.03	0.25	0.04	0.2	0.07	0.3	
Benzo(b)naphtho(2,1-d)thiophene							

Particulate matter, mg/SCM:	8	6	458	176	8	197
Extractable organics, mg/SCM:	3	2	96	128	8	66
Percent Bap in particulate matter:	0.001	0.001	0.024	0.030	0.002	0.06

- a. Emissions samples with modified EPA method 5 train; samples extracted with dichloromethane (filter reextracted with toluene) and analyzed for PAH by GC/MS; Reference 93.
- b. Magazine-type coal stove; with bituminous coal, some exhaust gas passed through magazine of fuel.
- c. Batch feed type stove which can be used for wood or coal.
- d. Reference 94; free standing air jacketed stove originally designed as a fireplace insert; EPA modified method 5 sampling.

liquid chromatography and analyzed for PAH by GC/MS. The ratios and emissions depend strongly upon type of coal, with much greater emissions of particulate matter, EOM and PAH observed with bituminous coal. With bituminous coal, the burn rate had little effect on the PAH ratios or on the percentage of BaP in the particulate matter. The ratios of PAH to BeP for the bituminous coal cover the same range as those reported by Grimmer *et al.* (71) for ambient samples collected in a coal-burning area of Essen, FRG, except for the chrysene ratio which was higher in Essen than in the emissions from the coal burning stoves.

Greater proportions of the lower molecular weight PAH, anthracene through chrysene, were observed with the anthracite than with the bituminous coal. The effect was greater for the high burn rate than the low burn rate.

Unfortunately, neither alkylated PAH nor sulfur-heterocyclics, which might provide the means for distinguishing emissions from coal combustion (73) from other sources were measured by Sanborn *et al.* (93). The ratio of benzo(k)fluoranthene to BeP, however, was higher in the emissions from coal combustion than in the tunnel samples (Table 4-3). The ratios of fluoranthene to pyrene in the coal combustion emissions were all less than 1.8, regardless of coal type as compared to ratios greater than 2.7 for the emissions from oil-burning residential furnace. Here again the data are limited to very few samples but are suggestive of some potential for distinguishing certain sources.

4.3.5 Residential Wood Combustion

A number of papers and reports (27, 28, 94-104) were reviewed in an attempt to define the PAH emission profiles from the combustion of wood in stoves and fireplaces. Unfortunately, the review provided few papers that had extensive profiles and only three included analyses of BeP (94-96). The ratios of the selected PAH compounds to that of BeP for the three above mentioned studies are found in Table 4-10. The Table is divided according to fuel type, i.e., oak and pine. The most conventional models of burning are side draft and up draft; therefore, columns one, two, five and six of Table 4-10 should be examined first. For the higher molecular weight compounds beyond benz(a)anthracene most ratios were within a factor of 3, with the greatest divergence coming from the data reported by Truesdale et al. (94) in column six for benzo(ghi)perylene. There is no obvious reason for this discrepancy since the sampling and analytical techniques were similar. For the lower molecular weight PAH, the ratios varied by as much as an order of magnitude.

The data in columns three and four were for initial conditions designed to improve the combustion of the wood and reduce emissions. the down draft technique decreased the actual emissions of PAH substantially. In addition, the PAH/BeP profiles changed dramatically, with much higher proportions of anthracene through chrysene being produced. A similar result occurred for the highly turbulent fuel burn, column four.

Table 4-10. Ratios of PAH to Benzo(e)pyrene in Emissions from Residential Wood Combustion

Fuel:	Seasoned Oak						Pine	
Burn mode: ^{a.}	Side ^{b.} Draft	Up Draft	Down ^{b.} Draft	High Turbulence ^{b.}	c.		Side ^{d.} Draft	c.,e.
Reference:	95	95	95	95	94	96	95	94
Anthracene	4.8	1.1	20	2.8	12	3.4	2.7	7.5
Phenanthrene	17	4.8	175	44	20	4.8	14	12
Fluoranthene	5.5	2.2	124	16.9	7.4	2.2	1.9	4.7
Pyrene	3.0	1.7	69	10.8	5.2	1.7	1.3	3.7
Benzo(c)phenanthrene								
Benz(a)anthracene	1.8	3.2	11.4	3.0	0.1	3.2	0.45	1.3
Cyclopenta(cd)pyrene								
Chrysene	1.8	2.0	15.7	2.8	3.2		0.47	0.6
Benzo(b)fluoranthene	{ 4.0	{ 4.3	{ 6.9	{ 1.9	{ 4.3		{ 3.0	<
Benzo(k)fluoranthene								
Benzo(j)fluoranthene								
Benzo(e)pyrene	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Benzo(a)pyrene	1.4	3.0	0.49	1.0	1.2	3.2	1.8	0.9
Perylene	0.16	0.19	0.33	1.0	1.6		0.26	0.11
Benzo(ghi)perylene	5.9	1.0	0.40	1.4	0.08	1.0	4.2	0.11
Indeno(1,2,3-cd)pyrene	4.1	1.2	0.58	2.0			5.3	
Coronene	2.7	0.25	0.31	1.6	<	0.25	2.2	0.22
Anthanthrene								
Benzo(b)naphtho(2,1-d)thiophene								

a. Related to stove design.

b. Samples collected with modified EPA method 5 sampling train (XAD resin bed); extracted with dichloromethane; ratios for gaseous plus particulate PAH given.

c. Free-standing air-jacketed open fire box originally designed as a fireplace insert; modified EPA method 5 sampling train used; extraction solvent not reported.

d. Green pine.

e. Copper-treated pine lumber.

The comparison with the emission tests for green pine are found in the last two columns of Table 4-10. Truesdale et al. (94) used treated pine, while Cook et al. (95) used green pine. The ratios for pine generally fall within the ranges observed for seasoned oak. This is due to the wide ranges observed for the seasoned oak.

Compared to the PAH profiles examined for other combustion emissions, there appears to be a much wider variation in the PAH profiles of the source emissions from wood burning stoves and a greater dependency on combustion conditions. None of the reported profiles would appear to represent a suitable average for this type of source. There is further evidence of this in the results of Imhoff and co-workers (97). These investigators sampled the ambient aerosol in a town in Alabama with about 1200 homes, of which 880 were estimated to be equipped for woodburning. Ambient samples were collected on a filter followed by an XAD-2 resin bed to trap more volatile PAH. A dispersion model was used with the PAH emission factors reported by Manning and co-workers (96) to predict ambient concentrations of PAH and the predicted concentrations were compared with those actually measured. The emission factors were not generated at the study site. Some of these results are shown in Table 4-11. The model under predicted ambient concentrations of PAH by about an order of magnitude or more. Of more significance from the point of view of receptor modeling, the profile of the PAH for the ambient average concentrations differed considerably from that of the source profile. Most of the ratios were

Table 4-11. Measured and Dispersion Modeled Concentrations of PAH (and their Ratios to Benzo(e)pyrene)^a.

Compound	Average Measured Concentration ng/m ³ (PAH/BeP)	Emission Factor ^b . mg/kg (PAH/BeP)	Modeled Concentration ng/m ³
Anthracene	53 (0.3)	1.49 (4.8)	2.7
Phenanthrene	1040 (5.6)	2.10 (3.4)	11.6
Fluoranthene	98 (0.5)	0.99 (2.2)	5.5
Pyrene	146 (0.8)	0.75 (1.7)	4.1
Benz(a)anthracene	76 (0.4)	1.40 (3.2)	7.7
Benzofluoranthenes ^c	89 (0.5)	1.90 (4.3)	10.5
Benzo(e)pyrene	187 (1.0)	0.44 (1.0)	2.4
Benzo(a)pyrene	52 (0.3)	1.40 (3.2)	7.7
Benzo(ghi)perylene	89 (0.5)	0.46 (1.0)	2.5
Coronene	51 (0.3)	0.11 (0.25)	0.6

a. From Imhoff et al. (1982), Reference 97.

b. Data from Manning et al. (Reference 96) used by Imhoff et al. (97).

c. Isomers not resolved.

lower for the ambient samples than for the source profile.

Contributions from motor vehicles may have contributed to an altered ambient aerosol profile but this should raise the ratios for coronene and benzo(ghi)perylene. The sample collection method, in which particles were collected on a hot filter and PAH collected separate from the particles on an XAD resin bed, could also have affected the observed profile. That is, the profile of the PAH after adsorption on the soot particles (as they are found in the atmosphere) may differ from that of the gaseous emissions samples on an XAD resin trap.

Although the data available for PAH emissions from residential woodburning are not useful for receptor source apportionment modeling, it may be possible to distinguish contributions from this source-type by using a profile which represents "average" conditions for a given site or by means of unique markers. Unique markers are discussed in Section 4.8.

4.3.6 Oil- and Coal-Fired Power Plants

Few data are available for calculating PAH ratios to BeP in emissions from power plants (57, 105-109). Concentrations of PAH in the particulate emissions from these source types have been shown to be in the ppb range (57, 105) making it difficult to collect sufficiently large samples for analyses. As a consequence, concentrations of the high molecular weight PAH compounds, such as BeP, are often below the limit of detection. Since there are so few data, data from the 1960's, reported by Cuffe, Gerstle and co-workers (57, 106, 107), have been

included in Table 4-12. In most instances, the data included in Table 4-12 involved collection of vapor phase PAH separate from particles with either condensation traps (108, 109) or XAD-2 resin (107). Natusch (108) did not report sample collection methods but the stack sample was probably collected in a manner similar to that used by others (105-109); the plume sample presumably was collected on a filter with no back-up collector for vapor phase PAH.

Bennett and co-workers (105) sampled one oil-fired and three coal-fired power plants. For most samples, concentrations of PAH beyond the molecular weight of pyrene were generally below the limits of detection. Five samples were collected at the oil-burning power plant but only one sample had high enough concentrations of all PAH to calculate ratios to BeP; this sample was collected when a high sulfur-high V residual oil was being burned. The ratios to BeP for this sample, shown in the first column of Table 4-12, ranged from 15.6 for phenanthrene/anthracene to 0.04 for indeno(1,2,3-cd)pyrene.

Ratios of PAH to BeP for coal-burning power plants, based on the measurements of Cuffe, Gerstle et al. (106, 107) are shown in columns 2 through 5 of Table 4-12. Duplicate samples collected at unit D (columns 4 and 5) suggest that, for a given plant, the ratios are fairly reproducible. The PAH profiles from different plants, however, varied over an order of magnitude in some instances.

The last two columns of Table 4-12 present the data of Stahley reported by Natusch (108) for samples collected in the stack of a plant

Table 4-12. Ratios of PAH to Benzo(e)pyrene in Emissions from Oil- and Coal-Fired Power Plants

Fuel:	Oil ^a .	Coal ^c .	Coal ^c . Unit C	Coal ^{c,d} . Unit D	Coal ^{c,d} . Unit D	Coal In Stack	Coal In Plume 0-5miles
Reference:	105	106	107	107	107	108	108
Anthracene	nr { 15.6	0.42	0.06				
Phenanthrene		3.2	0.38				
Fluoranthene	3.2	6.5	4.7	0.5	0.4	0.3	0.3
Pyrene	3.9	3.4	1.7	0.3	0.5	1.7	3.8
Benzo(c)phenanthrene	0.5						
Benz(a)anthracene	b.		1.9			7.0	14.7
Cyclopenta(cd)pyrene							
Chrysene	0.7 ^b .					4.9	4.3
Benzo(b)fluoranthene	nr { 1.6						
Benzo(k)fluoranthene							
Benzo(j)fluoranthene							
Benzo(e)pyrene	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Benzo(a)pyrene	0.4	1.7	1.7	0.3	0.2	1.3	1.0
Perylene	0.1	0.3	0.8			<0.2	0.4
Benzo(ghi)perylene	0.08	0.65	1.8	1.5	1.8	1.2	0.8
Indeno(1,2,3-cd)pyrene	0.04						
Coronene	0.05	0.02	0.08	0.22	0.17		
Anthanthrene		0.1	0.06				
Benzo(b)naphtho(2,1-d)thiophene							
Particle Concentration, mg/m ³	471		527	1557	550		
BaP in particles, ppb	5						

nr-not resolved.

- a. Venezualan residual oil, high S (2.4%) and high V (590 ppm) used.
- b. Chrysene + benz(a)anthracene.
- c. Eastern U.S. Bituminous coal.
- d. Duplicate samples from Unit D.

and in the plume. The ratios for pyrene and benz(a)anthracene were twice as high for the plume as for the stack sample. Assuming conventional stack sampling methodology, this suggests that ratios of PAH may change when PAH emissions have cooled and been adsorbed on emitted coal fly ash particles.

Comparisons between the ratios in Table 4-12 and those for other source types are difficult since there are so few compounds and samples. The ratios of the low molecular weight PAH in the emissions from the coal burning power plants appear to be lower than those observed for condensate samples from spark-ignition gasoline engines (Table 4-4); there are some similarities to the PAH profiles for emissions from residential bituminous coal burning (Table 4-9). For residential coal burning, however, benzo(a)pyrene ranged from 0.02 to 0.06% of the particle mass while this compound is in the ppb range for emissions from the more efficient power plants.

4.3.7 Industrial Coal Fired Boilers

Burlingame and co-workers (110) have recently sampled emissions from eleven coal stoker fired industrial boilers using state-of-the-art methods for sampling and analysis. Samples were collected with a modified SASS train, using XAD-2 resin to trap the PAH compounds. The samples were extracted with dichloromethane, fractionated on silica gel and the PAH compounds were analyzed by capillary gas chromatography-mass spectrometry. Concentrations of trace elements were also determined. The ratios to BeP for samples for which BeP data were available are

presented in Table 4-13. The letters B, C, etc., designate different sites while the numbers are sample numbers. Data for two samples at the same site were available in several instances.

Among different PAH measured for a given sample, the ratios vary over more than two orders of magnitude. For samples collected at the same plant the ratios to BeP were in very good agreement. However, the ratios varied more widely between boilers. The smallest boilers, H 11 and K 18 consistently exhibited the lowest PAH ratios. With the exception of H 11 and K 18 there was a consistent pattern of very high proportions of phenanthrene and fluoranthene in the emissions from these sources. The data reported by Bergstrom et al. (111) for coal fired industrial boilers also show this pattern (ratios could not be computed since BeP was not determined).

4.3.8 Emissions from Coke Ovens

Bjorseth and co-workers (112) sampled emissions at a coke plant in Norway during two seasons in 1976. The ratios of PAH to BeP (vapor plus particulate) for the stationery and mobile samples are summarized in Table 4-14. Stationary samples were collected on top of the coke oven batteries on Acropore filters each backed by two absorption bottles with ethanol cooled with dry ice. The typical sample size was 1 m^3 . Thirteen samples were collected in the spring and 10 in the fall; average concentrations were reported. The equipment for the mobile samples was similar with a typical sample size of 0.5 m^3 . The ratios

Table 4-13. Ratios of PAH to Benzo(e)pyrene in Emissions from Industrial Coal Stoker Fired Boilers^a.

Boiler Capacity: Sample No.:	200,000	182,500	180,000	45,000	70,000	50,000			
Compound	B30	B33	C45	E16	E17	H11	J15	J16	K18
Anthracene	12.1	5.8	0.7	7.8	7.8	1.6	11	11	1.8
Phenanthrene	679	321	373	91	96	1.9	114	52	11
Fluoranthene	161	70	20	16	18	1.6	24	19	6.8
Pyrene	25	21	1.8	17	15	1.6	24	14	10
Benzo(c)phenanthrene	2.0	1.0	1.0	4.0	3.0	0.6			
Benz(a)anthracene	2.0	1.6	1.0	1.0	3.0	0.3			1.0
Cyclopenta(cd)pyrene									
Chrysene	2.0	3.4	1.5	5.2	7.0	2.6	2.0	2.0	1.0
Benzo(b)fluoranthene	{								
Benzo(k)fluoranthene		1.0	1.0	1.3		2.4	1.0	1.0	1.0
Benzo(j)fluoranthene									
Benzo(e)pyrene	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Benzo(a)pyrene	1.0	1.0		1.0		0.5			1.0
Perylene	1.0	1.0		1.0	1.0	0.5			1.0
Benzo(ghi)perylene			0.5	3.6	3.2	0.7	1.6	2.0	5.0
Indeno(1,2,3-cd)pyrene			0.5	4.4	3.0	0.6		2.0	2.0
Coronene	3.0			1.8	1.0	0.3	1.0	1.0	1.0
Anthanthrene									
Benzo(b)naphtho(2,1-d)thiophene									

a. Reference 110; eastern bituminous coal (12,000-14,000 BTU/lb) burned in all instances except C45; a western coal (8,500 BTU/lb was used at plant C.

for ambient samples collected in the area of Essen, FRG, with coke plants are included in the last column for further comparison.

The ratios in Table 4-14 for compounds beyond phenanthrene, generally agree within a factor of 3 across the two seasons. For anthracene and phenanthrene, the ratios to BeP determined by mobile sampling during the spring of 1976 were consistently lower than the other values but were closer to those determined for ambient samples near coke plants in Germany. The ratios for the ambient samples, in general, are slightly lower than those determined at the coke plant. This may be due to interferences from other sources in the ambient samples, differences between the emissions from the coke plants in the two countries or simply due to differences in sampling and analysis methods.

Bjorseth (113) has noted that the PAH profiles at the coke plant (112) were fairly constant as were those determined at a Soderberg aluminum reduction plant (114) and that emissions from the two sources could be distinguished. The PAH profile at the Soderberg plant had much higher proportions of phenanthrene and anthracene while the proportions of the benzofluoranthenes, benzopyrenes and coronene were about an order of magnitude lower, compared to the profiles for the coke plant (112).

Comparing the profiles from the coke plant emissions to those from the tunnel samples (Table 4-3) and automobiles (Table 4-4), it should be noted that the proportion of benzo(a)pyrene at the coke plant is generally higher than for the motor vehicles by a factor of two or more.

Table 4-14. Ratio of PAH to Benzo(e)pyrene in Emissions from Coke Plants

	Stationary Sampling ^a .			Mobile Sampling ^a .			Ambient Sampling in Area with Coke Oven ^e .
	Spring, 1976 ^b .	Fall, 1976 ^b .	Spring, 1976 ^c .	Spring, 1976 ^d .	Spring, 1976	Fall, 1976	
Anthracene	4.5	3.5	0.2	0.5	0.9	4.8	0.3
Phenanthrene	14.2	11.5	1.2	0.5	1.3	21.3	20.5
Fluoranthene	8.8	7.9	3.1	4.0	4.0	10.3	11.4
Pyrene	6.5	5.9	2.8	4.2	4.2	7.4	8.2
Benzo(c)phenanthrene	0.6	0.4	0.6	0.8	0.4	1.4	0.9
Benz(a)anthracene	1.5	3.2	1.6	1.6	1.6	2.9	4.8
Cyclopenta(cd)pyrene							
Chrysene/triphenylene	2.4	3.6	2.2	2.1	2.2	3.7	5.6
Benzo(b)fluoranthene							
Benzo(k)fluoranthene	nr		1.2	1.0	1.2	1.2	1.1
Benzo(j)fluoranthene							
Benzo(e)pyrene	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Benzo(a)pyrene	1.7	2.0	1.8	1.9	1.5	2.1	2.3
Perylene	0.3	0.4	0.4	0.5	0.4	0.5	0.5
Benzo(ghi)perylene	0.5	1.3	0.5	0.6	0.5	1.1	1.2
Indeno(1,2,3-cd)pyrene							
Coronene	0.5	0.3	1.0	0.8	0.8		0.6
Anthanthrene	0.4	0.8	0.5	0.6	0.4	0.4	0.8
Benzo(b)naphtho(2,1-d)thiophene							0.07
							0.35
Particle concentration, mg/m ³	10.2	6.4	4.0	11.87	11.70	5.76	7.21
%BaP in particles	0.54	0.58	0.20	0.48	0.10	0.14	0.20

nr-not resolved.

- Bjorseth et al. (1978), Reference 112; samples collected on Acropore filters backed by 2 absorption traps with ethanol at dry ice temperature; extracted with cyclohexane; after clean-up, samples analyzed by capillary GC.
- On battery top.
- Outside larry car, on battery top.
- In larry car cabin on battery top.
- Grimmer et al. (1980), Reference 71.
- Chrysene alone.

The proportions of benzo(ghi)perylene and benzo(c)phenanthrene are higher for the tunnel and automotive exhaust samples than the coke plant samples, although there is only a single tunnel sample for the last compound. Thus, it may be possible to distinguish these two source types. Distinguishing emissions from coke ovens from those from space heating by means of PAH profiles may be more difficult. The proportions of benzo(a)pyrene and anthanthrene appear to be higher in the coke oven emissions than in emissions from residential coal combustion (Table 4-9) but the ambient data of Grimmer *et al.* (71) (Table 4-2) is inconsistent with this pattern. It should be noted that the concentrations of the PAH compounds in the particles from the coke plants are much higher than for other sources; benzo(a)pyrene ranged from 0.1 to 0.6% of the particle mass in coke plant aerosol (Table 4-14) as compared to less than 0.04% for tunnel samples (Table 4-6) and 0.001 to 0.06% for residential coal combustion. This enrichment in PAH should enhance the potential for distinguishing this source from others.

4.3.9 Resuspended Soil

Resuspended soil generally constitutes a significant fraction of total suspended particulate matter (TSP) in urban atmospheres. Evans and Cooper (115) have estimated that open sources in the U.S., such as unpaved roads, cropland, etc., may contribute about forty times the mass emitted by other anthropogenic sources of TSP. Receptor source apportionment models indicate that resuspended soil typically contributes 10 to 50% of the TSP in urban areas (1-6, 116). Since urban

soils and road dust can be contaminated with PAH from combustion sources, it is appropriate to try to estimate the concentration of airborne PAH which might be associated with this source. Shabad (117) has reported upper limit concentrations of 1-2 ppm BaP in urban soil; Grimmer (118) measured 1.5 and 3 ppm of BaP in soil samples from a bus stop and a highway, respectively. Lower levels are typically reported for non-urban soils (119). Assuming that 10 to 30 $\mu\text{g}/\text{m}^3$ of the urban aerosol is resuspended soil and using the higher concentrations of BaP in soil, then approximately 0.01 to 0.1 ng/m^3 of BaP might originate from this source. Differences between the particle size distributions of soil and resuspended oil have not been considered; if PAH compounds are concentrated in the smaller soil particles which can be resuspended, then this source could be more important than indicated by the foregoing calculation.

Only two reports of multiple PAH compound analysis was found during this review. Wang and Meresz (120) measured PAH at the surface of soil collected 50 m from one of Canada's busiest highways in Toronto. Although the sample was not size-classified prior to analysis, the relative proportions of PAH should be independent of particle size. Butler and co-workers (121) measured the PAH content of the surface soils in the vicinity of a heavily traveled motorway interchange in England. These data are presented in Table 4-15. The profile of the PAH compounds for any given sample is rather flat with ratios generally varying within a factor of three among the measured compounds. There

Table 4-15. Ratios of the Concentrations Polycyclic Aromatic Hydrocarbons to Benzo(e)pyrene in Soil Near Roadways^{a, b}.

Compound	Ratios to BeP								
Anthracene	0.4								
Phenanthrene	0.4								
Fluoranthene	1.2	1.3	1.2	1.7	3.7	2.5	1.2	1.6	1.2
Pyrene	0.9	1.5	0.9	1.9	2.5	2.3	1.9	2.0	0.8
Benzo(c)phenanthrene	-								
Benz(a)anthracene	0.8	1.4	1.0	2.9	1.7	2.0	2.0	1.4	0.8
Cyclopenta(cd)pyrene	-								
Chrysene	0.8	1.3	1.5	2.3	1.8	1.1	1.8	1.2	1.6
Benzo(b)fluoranthene	0.8								
Benzo(k)fluoranthene	0.5								
Benzo(j)fluoranthene	-								
Benzo(e)pyrene	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Benzo(a)pyrene	0.9	0.9	1.0	1.0	0.7	1.0	0.8	1.4	1.0
Perylene	0.3								
Benzo(ghi)perylene	1.3								
Indeno(1,2,3-cd)pyrene	0.7								
Coronene	0.5	0.1	0.4	0.4	0.2	0.3	0.1	0.1	0.1
Anthanthrene	0.3								

- a. The first column presents data from Reference 120; benzo(e)pyrene concentration was 0.116 $\mu\text{g/g}$. soil.
- b. All other ratios are based on data reported in Reference 121; concentrations of BeP in soil ranged from 0.16 to 2.3 $\mu\text{g/g}$. soil.

was a similar variation among samples in the ratios. The profiles differ somewhat from those of aerosol samples collected in tunnels (Table 4-3) and from motor vehicles (Table 4-4); the latter generally show higher proportions of chrysene and benzo(ghi)perylene. This may be due to reactions of PAH on deposited particles from motor vehicles or to the presence of PAH produced by geochemical or biological processes (119). Additional measurements of PAH in resuspended soil would be of value.

4.4 ALIPHATIC HYDROCARBONS

Aliphatic hydrocarbon (which include alkanes, alkenes, terpenes, etc.) generally constitute 20-65% of the non-polar organic compounds in urban aerosols (15, 122-124). These compounds originate from both anthropogenic (e.g., combustion) (32) and natural (e.g., plant waxes) sources (15, 30). Wynder and Hoffmann (15) first suggested that the relatively unreactive particulate alkanes might be useful in identifying major sources of air pollutants but there have been few measurements of these compounds in source emissions.

The n-alkane distribution of ambient aerosols dominated by contributions from plant waxes have been found to exhibit a strong odd-to-even carbon number preference (30, 125), i.e., the proportion of odd carbon number n-alkanes are greater than those of the even number homologs. Wind abrasion of leaves can lead to the formation of airborne wax particles (30, 125). These waxes are a complex mixture of n-alkanes, fatty alcohols, fatty acid esters and other compounds (125, 126); the n-alkanes are typically dominated by the odd carbon

number homologs (30, 125-127). Simoneit and Mazurek (125) have measured these compounds in aerosols collected in the rural western U.S. and in Los Angeles and estimated that aerosol concentrations of the n-alkanes, fatty acids and alcohols from plant waxes ranged from 0.03-0.46 $\mu\text{g}/\text{m}^3$. Similar values come from Wils *et al.* (126) who estimated that plant waxes contributed 0.03 to 0.1 $\mu\text{g}/\text{m}^3$ to the urban aerosol in Delft, Holland during the summer of 1981. Although it may be possible to estimate contributions to the urban aerosol from plant waxes using n-alkane profiles or the carbon preference index (30, 125, 126), it should be kept in mind that this source appears to contribute only a small fraction of the urban aerosol, even during summer (125-127).

There have been few measurements of n-alkanes in source emissions (122, 128) and consequently comparisons among sources cannot be made. The few data available for source emissions, as well as ambient measurements, indicate that the relative concentrations of the particulate C_{24} to C_{36} n-alkanes vary over only one order of magnitude and thus may be less useful than the PAH compounds in distinguishing combustion sources. However, there have been few reported measurements of vapor phase plus particulate n-alkanes for the C_{24} through C_{36} compounds which would be of interest; inclusion of volatile n-alkanes would extend the range of relative concentrations.

Based on currently available data, it appears that the n-alkanes may be most useful in distinguishing contributions from plant waxes from anthropogenic sources of aerosol. However, individual marker compounds, such as the phytosterols (129), which also originate from plants, may be simpler to use for this purpose.

4.5 NITROGEN-CONTAINING ORGANIC COMPOUNDS

4.5.1 Aza-arenes

The aza-arenes, heterocyclic nitrogen compounds, are present in urban aerosols at concentrations that are generally 1-2 orders of magnitude lower than those of the PAH (130, 131). There have been relatively few measurements of this class of compounds in either the ambient aerosol or in source emissions (32). Sawicki and co-workers (130) measured concentrations of aza-arenes in air contaminated by coal tar pitch, in emissions from a residential coal furnace and in effluents from an oil refinery. The ratios of the concentrations of these compounds to that of benzo(e)pyrene, determined by Sawicki *et al.* (130) have been summarized in Table 4-16. These ratios suggest that there may be significant differences among these sources that would be useful in distinguishing them. Although similar data are not available for automotive exhaust, the nature of the fuel suggests that the ratios to BeP in the emissions from spark-ignition engines should be low. Additional measurements for these source types as well as others would be required to determine whether this class of compounds might be useful in distinguishing sources. It should be kept in mind that the levels of the aza-arenes are lower than those of the PAH compounds in ambient aerosols and consequently larger samples would be required for analysis.

4.5.2 Nitro-Polycyclic Aromatic Hydrocarbons

The nitro-PAH compounds have been the focus of intense study over the past few years due to their mutagenic behavior, their presence in

Table 4-16. Ratios of Some Aza-Arenes to Benzo(e)pyrene in Source Emissions^a.

Compound	Residential Coal Burning	Ratio x 10 ² Oil Refinery Samples		Coal Tar Pitch Polluted Air
Acridine	22.9	0.3	1.5	370
Benzo(f)quinoline	11.5	7.6	3.2	180
Benzo(h)quinoline	7.5	16.1	9.4	110
Phenanthridine	6.5	16.1	5.5	95
Benz(a)acridine	5.2	0.6	0.4	86
Benz(c)acridien	2.9	1.5	1.4	52
Dibenz(a,h)acridine	3.3		0.01	4.3
Dibenz(a,j)acridine	0.4		0.04	0.5
Concentration of BeP, mg/g BSO ^b .	4.8	3.3	31.0	2.1

a. Sawicki et al. (1965) Reference 130.

b. BSO = benzene-soluble organics.

diesel exhaust and projections that up to 10% of new U.S. passenger cars could be diesel powered by 1985 (132). As a consequence most of the measurements of these compounds have been made on motor vehicles. Some of the available data on 1-nitropyrene (1NP) and 6-nitrobenzo(a)pyrene (6NBP) are compared in Table 4-17. The concentrations ($\mu\text{g/g}$. particles) of these two compounds in samples of exhaust collected from dilution tunnels in laboratories were about an order of magnitude higher than those determined for woodburning and a coal fired boiler, suggesting that such compounds might be useful in tracing motor vehicle emissions. However, there are measurements for only two other sources.

Furthermore, there is now some evidence that some of the nitro-PAH in laboratory dilution tunnel samples is artifactual. Gorse and co-workers (50) determined concentrations of 1NP in samples collected in the Allegheny Mountain Tunnel and, using traffic counts, estimated the contributions of diesels and spark-ignition engines. The concentrations of 1NP determined this way (shown in Table 4-17) were about an order of magnitude lower than those determined in laboratories. This is probably a consequence of greater dilution ($\sim 10^3$ within a few seconds) of the emissions in the tunnel as compared to the laboratory and decreased rates of PAH nitration (50).

Based on the very limited source emissions measurements currently available, it is not possible to judge whether 1NP or other nitro-PAH might be used to identify emissions from motor vehicles. The similarity of the concentrations in the tunnel samples and in the two other sources

Table 4-17. Concentrations of Two Nitro-Polycyclic Aromatic Hydrocarbons in Source Emissions and in the Ambient Atmosphere

Source	n*	µg compound per g. particles			Ref.
		1-nitropyrene	6-nitro-BaP	BaP	
<u>Motor Vehicles</u>					
Leaded gasoline ^a .	2	3.9 ± 1.3	33 ±16	61.2±0.7	133
Unleaded gasoline ^a .	3	4.3 ± 3.2	17 ± 8	179 ±5	133
Catalyst car ^a .	2	0.6 ± 0.5	0.2 ± 0.1	3 ±3	133
Diesel car ^a .	4	8 ± 2	<0.4	2.2±0.4	133
5 Diesel cars ^a .	5	10 ± 8	1 ± 1	-	134
4 Diesel engines	4	0.45±14.7			135
<u>Fireplace, red oak^b.</u>	2	0.11± 0.02	0.12± 0.01	60 ±16	134
<u>Coal-Fired Boiler</u>		0.18	-	-	134
<u>On Road (Tunnel) Averages:</u>					
Diesel		0.54± 0.07	-	-	50
Spark-Ignition		<1.5			50

* n=number of samples collected from a single vehicle.

a. 8-fold dilution.

b. 25-fold dilution.

which have been measured do not suggest much potential use for this class of compounds.

4.6. CARBOXYLIC ACIDS

Aliphatic and aromatic carboxylic acids have been identified and quantitated in ambient urban aerosols by many investigators (15, 29-32, 136-142). Straight-chain aliphatic (fatty) acids in non-urban aerosols generally show higher proportions of even carbon number acids which are associated with biogenic sources such as pollen and fungal spores (30, 31, 142). Similar fatty acid distributions have been observed in urban and suburban aerosols, particularly during summer (137, 138), indicating the influences of biogenic sources. Atmospheric concentrations of these compounds in rural areas are generally in the ng/m^3 range while concentrations in urban aerosols are in the $\mu\text{g/m}^3$ range (31) indicating contributions from anthropogenic sources in urban areas. Very little information is available on fatty acid concentrations in source emissions although they have been identified in emissions from incinerators (32, 143), combustion of wood waste (32) and diesel engines (32).

Dicarboxylic acids have been identified in urban aerosols (139-141) and are believed to originate through the oxidation of cycloalkenes (140, 141). The particle size distributions and diurnal variations in the concentrations of dicarboxylic acids measured during photochemical smog episodes (139, 140) as well as their formation in smog chamber experiments (141) are evidence of the secondary nature of these compounds. The dicarboxylic acids, thus, may be useful in estimating secondary organic aerosol concentrations. However,

combustion source emissions have not been examined for the presence of these compounds; this would be necessary before attempting to use them as secondary organic aerosol tracers.

Aromatic acids have been identified in urban aerosols and there is evidence that they can be formed through oxidation of gaseous organic compounds and gas-to-particle formation (139, 140). There are few measurements of these compounds in source emissions (32).

4.7 OTHER CLASSES OF ORGANIC COMPOUNDS

There are many other classes of organic compounds which have been identified in urban aerosols, e.g., aldehydes, ketones, quinones, nitro-aliphatics, phenols, halogenated hydrocarbons (12, 29-32). Measurements of these classes in source emissions, however, are too limited to make comparisons for the purpose of this review. The only other class which might be of interest with respect to source identification are the chlorinated aromatic hydrocarbons, e.g., polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins. These compounds are chemically stable and are emitted only by anthropogenic sources, as far as is known. Polychlorinated biphenyls, dibenzofurans and dibenzo-p-dioxins have been identified in emissions from incinerators (32, 143, 144). The generation of these compounds is believed to be related to the chlorine content of the fuel, i.e., refuse. Such compounds might be useful tracers of incineration if emissions from other combustion sources can be shown to be lower per gram of particulate matter.

4.8 UNIQUE TRACERS

For receptor source apportionment models, a compound, element or isotope which is unique to one source or source type is ideal. There are several species which appear to be of this type.

Carbon-14 has been shown to be a valuable tracer for distinguishing emissions of contemporary carbon, such as woodburning, from those of fossil fuels (145-147). This isotope is present in all living matter in approximate equilibrium with the C-14 in the atmosphere which is continually being produced by cosmic rays. Because of β -decay, C-14 is essentially absent from fossil fuels. There are C-14 sources other than woodburning. Field burning, forest fires, vegetative emissions can also be sources of C-14 (145). Incineration of paper, which is a wood product, can also be a source of C-14. As with any tracer, a knowledge of the probable sources in a given area and some judgment are required for the use of this tracer in a receptor model. The sample sizes generally required for C-14 analyses are relatively large by air pollution standards but there are methods which require only microgram quantities (145) although the equipment for the latter is quite expensive.

Soderberg, Hornig and co-workers (148, 149) have recently reported that levoglucosan, the anhydride of β -glucose is a distinctive marker for wood smoke. This compound was identified in methanol extracts of ambient particulate matter collected in a woodburning area. The extracts were silated and analyzed by gas chromatography/mass spectrometry. Levoglucosan was present in particles produced by combustion of red oak at a high concentration, ~5%, but was absent in emissions from the combustion of western

coal. Earlier investigators had demonstrated that thermal decomposition of wood, cellulose or starch produced levoglucosan (150).

Ramdahl (151) has reported that retene (1-methyl-7-isopropylphenanthrene) is a molecular marker for combustion of spruce and resinous soft woods. It is believed to be produced by thermal degradation of abietic acid in resinous woods and appears to be absent from emissions from combustion of birch, straw, peat, coal, or oil (151). Although the yields of retene varied with combustion conditions, the concentrations were always similar to those of other PAH compounds (151). This compound has been detected in aerosols over rural western U.S. at concentrations ranging from 0.050 to 1.4 ng/m³ and was believed to originate from the natural degradation of abietic acid (125). Ramdahl (151) has reported ambient concentrations ranging from 6 to 8 ng/m³ for four samples collected in a woodburning area.

There are two other PAH compounds which may be almost unique tracers. Cyclopenta(cd)pyrene appears to be emitted in high concentrations from spark-ignition engines, based on the reports of Grimmer et al. (49, 71, 72). If it can be confirmed that emissions of this compound from other combustion sources are an order of magnitude lower relative to other PAH compounds, as suggested by the data of Grimmer et al. (71), (see Table 4-2), this compound may be useful as an "almost" unique tracer. Benzo(b)naphtho(2,1-d)thiophene may also be a useful tracer under certain conditions. This compound has been found in ambient aerosol samples collected in areas in which fuels containing sulfur were in use, e.g., coal, oil (71). It also appears to be emitted by diesel engines (72). In areas in which gas or wood are the principal fuels for

heating or during summertime, this compound may be useful in distinguishing emissions from diesel engines and spark-ignition engines.

Caffeine has been identified in the New York City atmosphere at levels 10 to 100 times higher than those of other nitrogen heterocyclic compounds (131). Coffee roasting plants in the New York-New Jersey area were inferred to be the source of this compound and thus, caffeine would be a unique tracer for such sources.

4.9 CONCLUSIONS AND RECOMMENDATIONS

4.9.1 Strengths of Existing Data

Despite their many limitations, the existing data provide some useful information with respect to receptor modeling. First, the PAH profiles of sources which have been repeatedly sampled and analyzed by the same investigators appear to be quite reproducible, e.g., coke oven (112), coal-fired boilers (110). Secondly, the existing data indicate that there are organic compositional differences which can be exploited for source differentiation. Furthermore, the data provide indications of which compounds should be investigated more fully. The PAH compounds in particular, appear most promising. Their proportions in emissions from a given source type frequently vary over several orders of magnitude which enhances their potential usefulness for source discrimination. There also appear to be several unique or almost unique PAH tracers which may be useful. The existing data provide a basis for selecting those compounds which are likely to be most stable in the

atmosphere. In addition, good sampling and analytical methods already exist for this class of compounds.

Finally, the interurban differences in PAH profiles which have been reported by Grimmer et al. (71) also indicate a potential for distinguishing sources on the basis of organic composition. More recently, Thrane and Wikstrom (152) have reported distinguishing the PAH contributions to the ambient aerosol from five source types including motor vehicles, space heating and aluminum plants through the application of a fuzzy clustering analysis to ambient PAH composition data.

4.9.2 Deficiencies of Existing Data

The existing data on the organic composition of source emissions have generally been collected for the purpose of determining emission rates and are clearly inadequate for use in receptor source apportionment modeling. The principal reasons for this are:

1. Limited and Incomplete Composition Data

Data generally exist only for the PAH compounds and even these have not been adequately measured in many sources of interest. The individual PAH compounds which have been measured were not always the same for each source tested. Other composition variables, e.g., other classes of organics, trace elements, carbon and particle mass have rarely been measured simultaneously for the same source.

2. Lack of Representative Average Composition Data

Existing organic composition data are rarely representative of the average emissions for a source type. Usually, they represent a single source and a single set of operating conditions for that source.

Differences in the sampling intervals used for ambient and source samples magnify their incompatibility for subsequent use in receptor models.

3. Incompatibility of Sampling Methods for Source Tests and Receptor Modeling Studies

Sampling methods used for source emissions are generally incompatible with those used for ambient samples collected at a receptor site. In the case of source sampling, organic vapors are frequently collected separately from emitted particles. For ambient samples, organic vapors are rarely collected with the particles. In addition, sampling duration (and filter loading) differ for the two types of samples which may also affect composition. Differences in the particle-size of the samples can also have a substantial impact on the measured composition.

4. Differences in Analytical Methods

The analytical methods and quality assurance practices used to collect existing source composition data vary widely. For receptor modeling, both accuracy and precision of the measurement are critical. This can be achieved for organic species only if samples are extracted and analyzed using the same methods, preferably in the same laboratory and with a quality assurance program.

4.9.3 Future Studies

In order to confirm that differences in organic source emissions exist which can be used for distinguishing sources and receptor modeling, it is recommended that a carefully designed winter experiment be conducted using the PAH as model compounds. Ambient and source (particle size-selective) samples should be collected at a site influenced by major source types, including automobiles, diesels, and oil heating. Source and ambient samples would have to be collected in such a way that the composition data would be comparable. Vapor phase and particulate PAH should be collected for all samples. The source emissions should be cooled and diluted to approximate that which occurs downwind of the source in the ambient atmosphere. The samples must be sufficiently representative of the average conditions of each source type. Sampler development work would be required to achieve this goal.

Ambient samples would be collected with size-selective samplers for carefully selected wind directions or at sites known to be dominated by emissions from a given source type. The latter type of samples would be compared to those collected by direct source sampling. Portions of the samples or matched samples would be analyzed for trace elements and other composition variables. All samples would be extracted (immediately) and analyzed by the same methods using best possible quality assurance practices. Such an experiment would determine if the organic composition of source emissions and the ambient aerosol could be

reconciled and which combinations of compounds and trace elements are most useful for distinguishing the sources.

This study will answer the following questions:

1. Can emission profiles of PAH compounds be successfully generated through direct source sampling that match the profiles of that source in the ambient atmosphere?
2. Can the PAHs be used to help distinguish emissions from different sources?
3. Can the PAHs be used to trace motor vehicle emissions in the near future when leaded gasoline is no longer used?

SECTION 5

DEVELOPMENT OF RECEPTOR SOURCE APPORTIONMENT MODELS FOR EXTRACTABLE PARTICULATE ORGANIC MATTER

5.1 INTRODUCTION

Previous work in this laboratory (7, 8) had indicated the feasibility of developing receptor source apportionment models for particulate extractable organic matter (EOM) and for polycyclic aromatic hydrocarbons (PAH). This work was limited by both the number of cases and the number of source tracer elements available for model development. As part of the present study, existing composition data for samples of respirable ($D_{50} \leq 3.5 \mu m$) particulate matter collected over a two year period at a single site in New York City were used for further study of organic source apportionment models. In addition, portions of these samples were analyzed for six additional trace elements by X-ray fluorescence spectrometry (XRF).

The factor analysis-multiple regression (FA/MR) modeling approach, which was developed and used previously in this laboratory (2, 5, 7, 8) was used to develop source apportionment models for particulate organic fractions and species. The lack of adequate organic source emissions data, as discussed in Chapter 4, precluded development of chemical mass balance models (1, 3, 4). This chapter presents the results of FA/MR modeling for three fractions of respirable EOM; work on target transformation factor analysis (153, 154), to develop source profiles, is in progress. Preliminary work done on models for two PAH compounds is presented in Appendix E. Further work on PAH compounds is in progress and will be reported at a later date.

5.2 EXPERIMENTAL

5.2.1 Sampling and Analyses

Weekly samples (two) of respirable ($D_{50} = 3.5 \mu m$) particulate matter (RSP) collected between 1/1/79 and 12/30/80 were collected and analyzed as described in Appendices B through D of this report. The samples were collected on the roof of a 15 story building located on the east side of Manhattan at the New York University Medical Center. The composition variables used in the development of the models, their mean values, standard deviations of the means and ranges, are presented in Table 5-1. Seasonal means for these variables are presented in Table 5-2. The concentrations of several variables (Pb, V, S) were determined by two different methods in two laboratories, as described in Appendix C. For four samples, the concentration of nickel was exceptionally high ($\sim 100 \text{ ng/m}^3$). For the factor analyses, cases for which Ni was greater than 100 ng/m^3 were omitted. The distribution of the cases among seasons is summarized in Table 5-3. There were 26 cases per season for spring, summer and fall and 24 cases for winter.

Most species did not show a seasonal difference in mean concentration (Table 5-2). The mean concentrations of RSPV, RV, RSPCYC, RSPACE, and RBR were higher during the heating season. Most of these variables are associated with oil burning. Nickel, generally associated with oil burning, did not show a significant seasonal difference in concentration. The lower summertime concentration of RBR, a tracer for motor vehicles, is probably associated with volatilization losses of

Table 5.1 Summary of Variables Used in Model Development, Their Means, Standard Deviations and Ranges

Symbol	Variable	n	ng/m ³		Range
			mean	± S.D.	
RSP ^{a.}	Respirable particles	99	31,790	±9,200	15,400-56,000
RSPPB	RSP lead	99	552	± 181	170- 1,150
RSPMN	RSP manganese	98	7.8±	2.5	3- 15
RSPCU	RSP copper	99	24.8±	14.4	5- 95
RSPV	RSP vanadium	99	47.0±	30.4	2- 124
RSPCYC	RSP cyclohexane-solubles	94	3,140	± 920	1,670- 6,330
RSPDCM	RSP dichloromethane-solubles	95	1,620	± 800	220- 4,100
RSPACE	RSP acetone-solubles	96	4,900	±1,650	1,580- 8,620
RSPSO ₄	RSP sulfate	97	8,390	±3,610	1,330-19,370
RS ^{b.}	RSP sulfur	98	3,840	±1,360	1,360- 8,740
RFE ^{b.}	RSP iron	98	348	± 106	162- 831
RPB ^{b.}	RSP lead	98	523	± 177	129- 1,169
RMO ^{b.}	RSP molybdenum	98	53	± 12	18- 81
RP ^{b.}	RSP phosphorus	98	67	± 29	29- 187
RBR ^{b.}	RSP bromine	98	103	± 57	33- 385
RV ^{b.}	RSP vanadium	98	42	± 23	12- 106
RTI ^{b.}	RSP titanium	98	16.5±	5.9	7- 36
RNI ^{b.}	RSP nickel	98	25.6±	37.8	3- 266
AVETEMP ^{c.}	average temperature	104	55.3±	17.8	12- 83.6

a. RSP = respirable (D₅₀ = 3.5 µm) particulate matter.

b. Determined by XRF analyses.

c. Degrees Fahrenheit.

Table 5-2 Seasonal Means $\pm$ S.D. of the Concentrations of Variables
Used for Model Development, ng/m³

Variable	Heating Degree Days ≥ 10 (n=49)		Heating Degree Days < 10 (n=34)	
RSPPB	569	$\pm$ 215	532	$\pm$ 135
RSPMN	8.1	$\pm$ 3.0	7.4	$\pm$ 1.7
RSPCU	24.9	$\pm$ 13.9	25.1	$\pm$ 15.7
RSPV	59.8	$\pm$ 30.3	33.8	$\pm$ 23.9
RSPCYC	3,450	$\pm$ 940	2,810	$\pm$ 770
RSPDCM	1,680	$\pm$ 890	1,610	$\pm$ 750
RSPACE	5,040	$\pm$ 1,680	4,820	$\pm$ 1,570
RSPSO4	6,700	$\pm$ 2,510	10,520	$\pm$ 4,170
RS	3,460	$\pm$ 1,070	4,440	$\pm$ 1,660
RFE	375	$\pm$ 105	322	$\pm$ 107
RPB	530	$\pm$ 197	504	$\pm$ 154
RMO	54	$\pm$ 10	54	$\pm$ 14
RP	70	$\pm$ 29	63	$\pm$ 24
RBR	117	$\pm$ 61	79	$\pm$ 35
RV	52	$\pm$ 23	33	$\pm$ 19
RTI	17	$\pm$ 6	17	$\pm$ 6
RNI	21	$\pm$ 14	17	$\pm$ 8

Table 5-3 Seasonal Distribution of Cases

^{a.} <u>Seasonal</u>	<u>Number of Cases</u>
Winter, 1979	8
Spring, 1979	13
Summer, 1979	13
Fall, 1979	13
Winter, 1979-1980	13
Spring, 1980	13
Summer, 1980	13
Fall, 1980	13
Winter, 1980	3

a. Winter - December, January, February;
 Spring - March through May;
 Summer - June through August;
 Fall - September through November.

bromine through chemical and photochemical reactions (19). Sulfate and sulfur concentrations were higher during the non-heating (summer) than during the heating season.

The distributions of the three EOM fractions were examined and are plotted in Figure 5-1. The data for RSPCYC and RSPACE appear to be normally distributed; at lower concentrations, the RSPDCM values show some deviation from a normal distribution.

5.2.2 Statistical Methods

The Statistical Package for the Social Sciences (SPSS, Version 8.3, was used for data analysis and model development (155). Factor analysis (principal factoring, R-type, Varimax rotation, minimum eigenvalue = 0.7) was used on the entire set of variables and on various subsets of the variables to identify independent source tracers. In the event of missing data for any variable in a case, the case was deleted from the set of cases.

Stepwise multiple linear regression models were then developed for each EOM fraction. These were of the form:

$$[EOM] = k_1 T_1 + k_2 T_2 + \dots k_i T_i + R \quad (1)$$

where [EOM] = the ambient concentration of the fraction of interest;

T_i = the ambient concentration of the source tracer;

k_i = the regression coefficient of source tracer T_i ;

R = the [EOM] not associated with the modeled sources.

The constants k_i relate source emissions to ambient concentrations according to the equation:

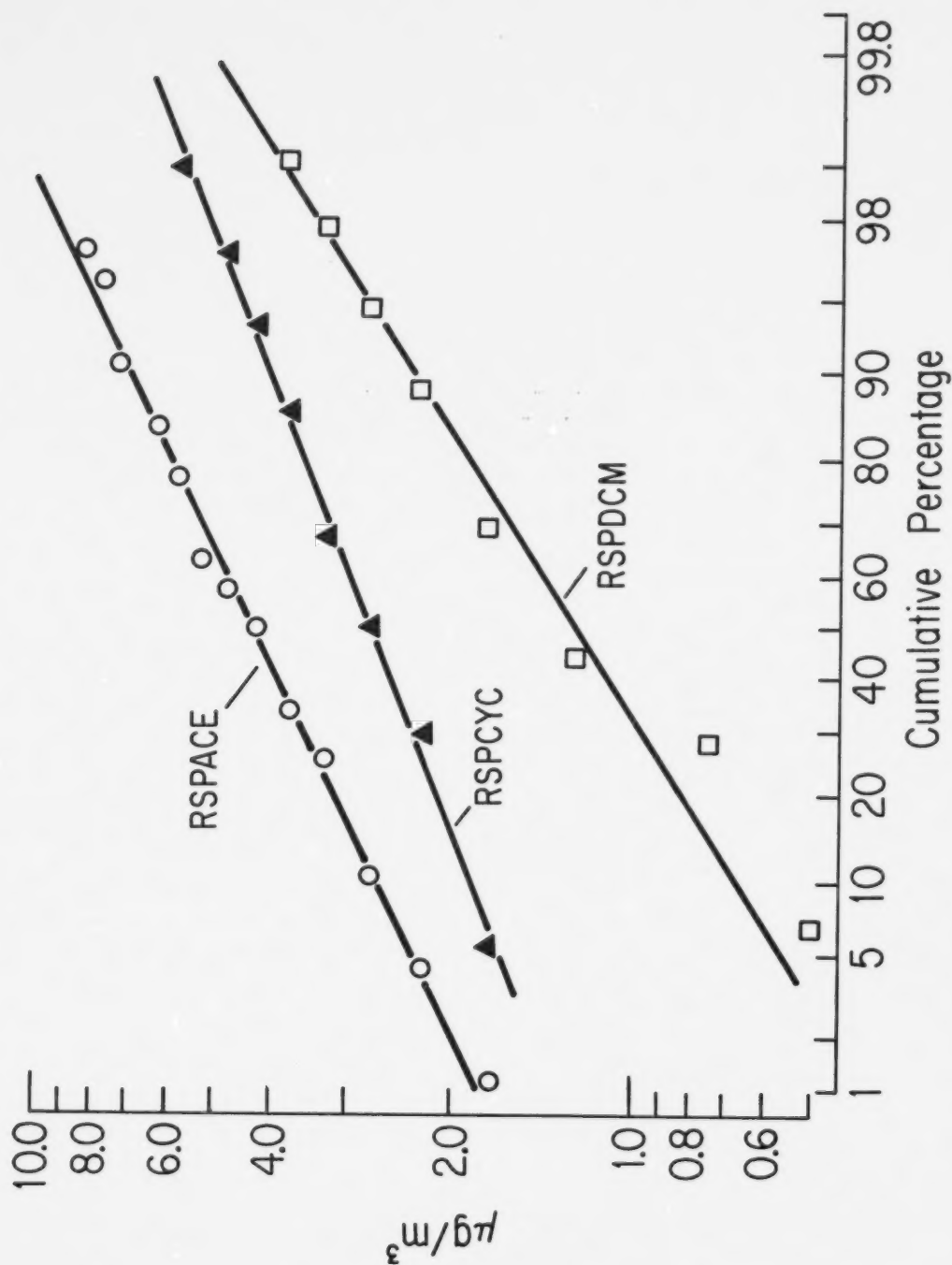


Figure 5-1. Distributions of measurements of RSPCYC, RSPDCM and RSPACE at the N.Y.U. Medical Center rooftop sampling station, New York City, 1979 and 1980.

$$K_i = \frac{\alpha_{ij} [EOM]_j}{T_j} \quad (2)$$

where $[EOM]_j$ = the concentration of EOM in emissions from source j ,

T_j = the concentration of the tracer element in emissions from source j , and

α_{ji} = the coefficient of fractionation which describes changes in the ratio $[EOM]_j/T_j$ which may occur between the source and receptor as the result of physical and chemical processes. The coefficients of the regression equations were compared with source emission data wherever possible for model validation.

5.3 RESULTS AND DISCUSSION

5.3.1 Factor Analysis

Tables 5-4 and 5-5 present typical results of factor analyses on trace elements and sulfate (all cases and only cases with RNI less than 100 ng/m³) Factor analysis was also performed on subsets of variables such as the trace elemental data, RSPPB through RSPSO₄ (NYU), and RS through RNI (EPA). In addition, since trace elemental data for total suspended particulate matter (TSP) were available, some factor analyses were done on subsets of variables which included coarse particle trace elements (calculated as the difference between TSP and RSP concentrations). Seasonal subsets of the variables were also factored and in one instance, factor analysis was done on trace elements, sulfate and EOM normalized to RSP mass. Six to nine factors were obtained,

Table 5-4 Related Factor Matrix for Trace Elements and Sulfate - All Cases (n=95)

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7
RSPB	.84484	.10878	-.04671	.06282	.14304	.10080	-.06881
RSPMN	-.03113	.40296	.53624	.16620	.17604	.08231	.29985
RSPCU	.13037	-.06186	-.00851	.00778	.44102	-.04323	-.06034
RSPV	.17182	.91233	-.00096	-.07799	-.07492	.13478	.06818
RSPSO4	.07963	-.33687	-.01018	.85500	.02568	.15020	.20334
RS	-.02809	.18457	.17169	.92186	.01613	.07970	.11657
RFE	.11832	.04641	.97515	.01231	-.07239	.07367	-.07668
RPB	.96095	-.03121	.05794	.18719	.15171	-.00191	-.09031
RMO	.02207	.05142	.25427	.19207	-.09780	.49578	-.11608
RP	-.11261	.58592	.28362	.05935	.37450	-.26380	.06633
RBR	.86832	.14523	-.08630	-.23564	-.02863	-.05971	-.09251
RV	.11777	.97494	.03622	-.03800	-.17641	.01157	-.05192
RTI	-.14659	.00124	.74309	.07043	.02820	.11355	-.00078
RNI	-.11003	.02171	-.00758	.13887	-.06786	-.07063	.39660

Eigenvalue ^a	2.97	2.56	2.15	1.34	0.59	0.24	0.15
Percent Variance:	29.7	25.6	21.5	13.4	5.9	2.4	1.5
Probable Source:	Motor Vehicles	Oil Burning	Resuspended Soil	Sulfate	Incineration	Molybdenum	Nickel

a. After rotation.

Table 5-5. Rotated Factor Matrix for Trace Elements and Sulfate^a.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7
RSPPB	.84748	.07998	-.04139	.07807	.04920	.12246	.08979
RSPMN	-.02071	.55615	.50524	.18281	-.16565	.11606	.08526
RSPCU	.10834	-.03891	-.01279	.01486	.06906	.58780	-.07521
RSPV	.17235	.83890	-.03731	-.10791	.35097	-.13128	.18886
RSPSO4	.07276	-.26936	-.00034	.89677	-.07640	.06165	.12682
RS	-.01873	.22286	.13836	.91054	.09128	-.01951	.09618
RFE	.11352	.06763	.98434	.00938	.01867	-.07319	.08850
RPB	.96142	-.05423	.06765	.19939	.02119	.13577	-.01254
RMO	.01494	.02935	.22970	.18620	-.04715	-.09976	.50069
RP	-.09268	.66654	.22785	.05637	.00008	.18906	-.30577
RBR	.88479	.09712	-.10022	-.23879	-.00958	-.06473	-.04901
RV	.12569	.86772	-.00195	-.09191	.35678	-.24789	.08260
RTI	-.14998	.05156	.72692	.06558	-.04519	.02174	.11005
RNI	.02092	.27226	-.05463	.02669	.64991	.11467	-.05742

Eigenvalue ^b .	3.04	2.51	2.22	1.39	0.66	0.40	0.22
Percent Variance:	29.2	24.1	21.3	13.3	6.3	3.8	2.1
Probable Source:	Motor Vehicle	Oil Burning	Resuspended Soil	Sulfate	Nickel	Incineration	Molybdenum

a. All cases (n = 91) for which RNI < 100 ng/m³.

b. After Varimax rotation.

depending upon the number of variable included. In all cases a consistent pattern emerged with the following sources being identified through the factor loadings on certain variables: (1) oil burning - RSPV, RV; (2) motor vehicles - RPB, RBR, RSPPB; (3) resuspended soil - RFE, RTI, RSPMN; (4) sulfate - RSPSO₄, RS; (5) incineration - RSPCU; (6) a nickel factor; (7) a molybdenum factor. The first four factors generally accounted for 80 to 90% of the total variance, while the incineration factor accounted for 4-5% of the variance. The nickel and molybdenum factors contributed only 1-3% of the variance and appeared to be of the type described by Roscoe et al. (156) as due to bias errors in the data. The limits of determination of these two variables were estimated to be 50 and 8 ng/m³ for RMO and RNI, respectively (R. Kellog, personal communication). Thus most of the values for RMO were below this limit while for RNI, 10% of the values were less than or equal to this value (17% of the RNI values were ≤ 10 ng/m³).

The element manganese was consistently split between the factors for oil burning and resuspended soil. This element is present in soil and in residual oil (which is a principal fuel in New York City). Phosphorus was also found in more than one factor. The highest loading was always observed for the oil burning (RV) factor with much lower (<0.3) with loading on the incineration and soil factors. If AVETEMP was included as a variable, a negative loading was observed on the oil burning factor.

In principle the dependent variables (RSPCYC, RSPDCM, RSPACE) should probably not be included in the factor analysis. However, it is of interest to examine their effect on the factor analysis and their association with the factors. The variables RSPCYC and RSPACE were consistently associated with oil burning and had fairly high loadings, although the loadings were slightly lower than those of RV and RSPV. A lesser association was observed for RSPCYC with the motor vehicle factor. The RSPACE had minor, although consistent, correlations with the factors for resuspended soil and sulfate. Recent work in New Jersey has indicated that under conditions of photochemical smog which result in formation of sulfate aerosol, secondary organic aerosol is found in the ACE fraction (157). The RSPDCM was generally found to be the most highly loaded variable in a separate factor which accounted for 3-7% of the variance in the data. The RSPCYC and RSPACE were also found in this factor but at lower loadings. This is probably due to their common extraction. The only other variables which showed some association with the RSPDCM were soil-related, e.g., RTI, coarse particle manganese.

Based on these factor analyses, the principal sources which were identified were oil burning, motor vehicles, resuspended soil, sulfate-related aerosol and incineration. These results are consistent with the initial work at this site by Kleinman et al. (2) as well as later analyses by Kneip et al. (5) and Daisey and Kneip (8).

5.3.2 Multiple Regression Source Apportionment Model for RSPCYC

In order to select source tracers for the multiple regression model for RSPCYC, correlations with individual tracers were examined as well as the associations of RSPCYC with the source factors. Associations with source factors could not be used as the sole indicator since the inclusion of other variables in the factor analysis tends to maximize association with one or two variables and minimize the associations with the minor source factors. The RSPCYC fraction was most highly correlated with RSPV ($r = 0.61$), RV ($r = 0.64$), RTI ($r = 0.41$), RFE ($r = 0.34$) and RPB ($r = 0.25$). Consequently, an equation of the form

$$[\text{RSPCYC}] = k_1[\text{RV}] + k_2[\text{RPB}] + k_3[\text{RTI}] + R \quad (3)$$

was postulated as Model I. The effect of substituting RFE as a soil tracer in place of RTI was also examined (Model II). The regression coefficients for these models are presented in Table 5-6. The values of F and r^2 for the overall equations are also presented. The coefficients for RV and RPB were both highly significant ($p \leq 0.03$) and similar to those reported previously (8). The coefficients for RTI and RFE were of marginal significance ($p \leq 0.135$) but were left in the equation. The coefficient for RTI was somewhat better statistically than that for RFE. The tolerance for each of the variables entered by the stepwise procedure was very high (≥ 0.98), i.e., there was little multicollinearity. (We note parenthetically that the tolerances

Table 5-6. Multiple Regression Coefficients of Models for RSPCYC^a.

Tracer Variable	Mean Concentration ± S.D., $\mu\text{g}/\text{m}^3$	Coefficients ± S.E. ^b	
		Model I	Model II
RV	0.0429 ± 0.0234	25 ± 3 (<0.001)	25 ± 3 (<0.001)
RPB	0.515 ± 0.179	1.06 ± 0.41 (0.01)	0.91 ± 0.40 (0.03)
RTI	0.0168 ± 0.0061	19.6 ± 12.0 (0.10)	-
RFE	0.352 ± 0.108	-	1.0 ± 0.7 (0.135)
R, $\mu\text{g}/\text{m}^3$		1.17 ± 0.33 (0.001)	1.24 ± 0.31 (<0.001)
Number of Cases		89	89
Overall r^2		0.48	0.48
Overall F		26.5	26.2
Significance		<0.001	<0.001

a. Coefficients for variable concentrations in $\mu\text{g}/\text{m}^3$.

b. Level of significance of coefficients given in parentheses.

observed for the dispersion normalized variables which have been used in past models were in the range of 0.6).

The coefficients determined for the 1979 and 1980 data have been compared in Table 5-7 to those determined previously at this site using measurements made in 1978. Ratios of non-polar extractable organics or of volatilizable carbon to each tracer for source emissions samples are also shown for comparison. The ratio of CYC to Pb for spark-ignition engines was based on cyclohexane extraction (at NYU) of Allegheny Tunnel samples provided by Dr. W. Pierson of Ford Motor Company. Portions of these samples were also analyzed for Pb. The mass of CYC and Pb emitted per km for spark-ignition engines was then estimated based on the percentage of diesel traffic (19). The estimates for spark-ignition engines were 9.3 and 4.75 mg/km for CYC and Pb, respectively. These data are in excellent agreement with those reported by Pierson and Brachaczek (19) for DCM-soluble organics (12 ± 3 , 5 ± 3 mg/km) and Pb (4.4 ± 0.7 mg/km) in the Allegheny Tunnel. In view of the possible differences between NYC and the tunnel in driving conditions and the mix of vehicles using leaded and unleaded gasoline, both ratios are reasonably close to that determined for Model I. An attempt was made to estimate a ratio of CYC/Pb for 13% diesel traffic and 87% spark-ignition traffic, which is a characteristic traffic mix for bridge and tunnel crossings into and out of Manhattan (159, 160) using the Allegheny Tunnel data (158). This estimated ratio was considerably higher than

Table 5-7. Comparison of Source Tracer Coefficients and Ratios of Non-Polar EOM or Volatilizable Carbon to Tracer in Source Emission

	Organic Species	Coefficient of or Ratio to:			Reference
		Pb	V	Ti	
Model I(1979,1980)	RSPCYC	1.1 $\pm$ 0.4	25 $\pm$ 3	20 $\pm$ 12	This work
Previous NYC Model (1978)	RSPCYC	0.65 $\pm$ 0.35	29 $\pm$ 4	-	5
Allegheny Tunnel, 1979					
Spark ignition engines ^a .	CYC	2 $\pm$ 7			158
Spark ignition engines	DCM(only)	1.1 $\pm$ 0.6			19
New York City Traffic Mix ^b .	CYC	$\sim$ 7			b.
Residual Oil(fine particle)	Volatilizable Carbon		5.7-34.0 0.6- 7.8 0.1-10.3		161 162 162
Street Dust(fine particle)	Volatilizable Carbon			11-31	162

a. Samples provided by W. R. Pierson, analyzed at N.Y.U.

b. Estimate based on Allegheny Tunnel data and New York City traffic mix (87% automobiles and 13% diesel trucks and buses; Reference 159, 160.

the coefficient for Pb but the uncertainty in the value is difficult to estimate.

Residual oil is the principle fuel used for power production and space heating in New York City. The coefficient for vanadium was within the range of ratios reported for residual oil burning. It should be noted that the ratios in the table are for volatilizable carbon which would be slightly lower than cyclohexane-soluble organics. The ratios to V can vary considerably depending upon the vanadium content of the residual oil. Kneip *et al.* (5) have reported changes in vanadium regression coefficients for TSP models in New York City which appear to be closely related to changes in the sources of crude oils used in New York City.

The coefficient for titanium is in very good agreement with the ratios calculated from the data reported by Watson (162) for fine particle road dust. Here again, volatilizable carbon rather than cyclohexane-soluble organics was measured. Since the non-polar organics extracted by cyclohexane are generally composed largely of compounds which have high percentages of carbon, e.g., alkanes (19, 163), the ratios for cyclohexane-soluble organics would be expected to be only slightly higher than those reported by Watson (162).

The source contributions to the ambient concentrations of RSPCYC, calculated using Model I, are presented in $\mu\text{g}/\text{m}^3$ and as percentages of the total in Table 5-8. Model II differed by only a few percent in estimates of the contributions of motor vehicles and soil. The three

Table 5-8. Source Contributions to RSPCYC Using Model I.

<u>Source</u>	<u>Tracer</u>	<u>$\mu\text{g}/\text{m}^3$</u>	<u>% of Total</u>
Oil Burning	RV	1.07 ± 0.13	34 ± 4
Motor Vehicle	RPB	0.55 ± 0.21	18 ± 7
Resuspended Soil	RTI	0.33 ± 0.20	10 ± 6
Residual	-	<u>1.17 ± 0.33</u>	<u>38 ± 11</u>
Total		3.12	100

sources, oil burning, motor vehicles and resuspended soil could account for 62% of the total RSPCYC with a remaining 38% which could not be accounted for by any of the other available tracers.

This remainder of unattributable fraction of RSPCYC, R, is relatively large compared to those obtained for TSP and RSP models (2, 5). One possible source contributing to the unattributed RSPCYC is the regional background of organic aerosol for which a tracer is lacking. This regional organic background is due to natural aerosols generated from such sources as plant waxes (30), resuspended soils, etc. as well as anthropogenic aerosols generated outside of New York City. Measurements made at two background sites in the region indicate that this regional background RSPCYC aerosol is of the order $0.8 \mu\text{g}/\text{m}^3$ (164). Measurements of RSPCYC made on monthly samples collected during 1979 and part of 1980 at a rural site in Tuxedo, N.Y., about 40 miles northwest of N.Y.C. ranged from 0.3 to $1.8 \mu\text{g}/\text{m}^3$ between January, 1979 and June, 1980.

Major urban areas located to the west of New York City would be expected to be more important contributors to N.Y.C. background organic aerosol. Although data are not available for any upwind urban sites for the 1979 through 1980 period, measurements made between 1981 and 1983 during the ATEOS study (13) can provide some indication of the significance of such upwind urban sources. The average concentrations of cyclohexane-soluble organics for two winter and two summer sampling campaigns were 5.4 and $3.0 \mu\text{g}/\text{m}^3$ at Newark and Elizabeth, N.J.,

respectively. These cities are located about 25 miles southwest of New York City. Such upwind sources might reasonably be expected to contribute $1.2 \mu\text{g}/\text{m}^3$ on average and thus account for the residual of the model. Contributions from such sources would be strongly dependent upon wind direction and weather and would vary from week to week.

Filter sampling artifacts must also be considered as potential contributors to the unattributed RSPCYC of the model. For the RSPCYC fraction volatilization losses would be expected to be significant for samples collected over a period of a week, even though the flow rate was lower (15 cfm) than is usual for most high volume sampling. If temperature were constant throughout the year, all samples would be equally affected and the model would be unchanged. Differences in filter loading from week to week might also result in a sampling artifact. Schwartz et al. (165) have presented data which suggest that condensation of vapor phase organics occurs to a greater extent on a more highly loaded filter and this would result in some uncertainty in the measured RSPCYC.

In regression analysis direct examination of residuals can often provide information on the adequacy of the model and whether the assumptions concerning the distribution of errors are met (166). The plot of the time sequence of the residuals of the RSPCYC model, shown in Figure 5-2, suggested some autocorrelation between cases; the Durbin-Watson statistic was 1.31 ($p = 0.05$) and the observed number of runs of signs was only 26 compared to the expected 45 (the probability of

Figure 5-2. Plot of Residuals of RSPCYC Model I as a Function of Time Sequence^a.

OBSERVATION	Y VALUE	Y ESTIMATE	RESIDUAL	-2SD	0.0	+2SD
106.	2.670000	3.703930	-1.033930			
107.	3.020000	3.325408	-.3054081		I	
108.	3.350000	3.676510	-.3465104		I	
109.	2.390000	2.980182	-.5901819		I	
110.	3.320000	3.414865	-.9486515E-01		I	
111.	4.690000	3.808701	.8812990		I	
112.	6.330000	4.701983	1.628017		I	
113.	3.580000	3.797653	-.2176531		I	R
114.	3.670000	4.192421	-.5224205		I	
115.	2.880000	3.426324	-.5463240		I	
116.	3.140000	3.592578	-.4525781		I	
117.	2.410000	3.236301	-.8263007		I	
118.	4.000000	4.536559	-.5365586		I	
119.	2.030000	3.049505	-1.019505		I	
120.	2.450000	3.129078	-.6790784		I	
121.	4.310000	3.616388	.6936115		I	
122.	2.730000	3.023615	-.2936155		I	
123.	2.640000	2.973337	-.3333368		I	
124.	CASE DELETED DUE TO MISSING DATA.				I	
125.	4.640000	2.672418	1.967582		I	R
126.	CASE DELETED DUE TO MISSING DATA.					
127.	CASE DELETED DUE TO MISSING DATA.					
128.	CASE DELETED DUE TO MISSING DATA.					
129.	CASE DELETED DUE TO MISSING DATA.					
130.	2.010000	2.538888	-.5288882		I	
131.	1.760000	2.122027	-.3620274		I	
132.	2.770000	2.832129	-.6212871E-01		I	
133.	2.950000	2.816302	.1336984		I	
134.	2.800000	3.142669	-.3426689		I	
135.	1.760000	2.952959	-1.192959		I	
136.	2.920000	3.044277	-.1242765		I	
137.	2.160000	2.376810	-.2168101		I	
138.	2.470000	3.019244	-.5492439		I	
139.	2.160000	2.723768	-.5637679		I	
140.	CASE DELETED DUE TO MISSING DATA.				I	
141.	CASE DELETED DUE TO MISSING DATA.					
142.	CASE DELETED DUE TO MISSING DATA.					
143.	2.730000	2.642309	.8769121E-01		I	
144.	2.690000	3.565265	-.8752652		I	
145.	2.470000	2.154944	.3150560		I	
146.	CASE DELETED DUE TO MISSING DATA.				I	
147.	4.040000	3.307164	.7328356		I	
148.	3.230000	2.903894	.3261059		I	
149.	3.680000	2.784545	.8954552		I	
150.	3.400000	2.857764	.5422365		I	
151.	5.760000	3.372399	2.387601		I	
152.	3.690000	3.015710	.6742897		I	R
153.	3.890000	3.006299	.8837007		I	
154.	3.690000	3.667056	.2294407E-01		I	
155.	4.450000	3.669055	.7809454		I	
156.	3.410000	3.883728	-.4737284		I	
157.	CASE DELETED DUE TO MISSING DATA.				I	

a. Case 106 = 1/4/79 to 1/11/79, Case 209 = 12/30/80 to 1/6/81.

Figure 5-2. Plot of Residuals of RSPCYC Model I as a Function of Time Sequence^a.
(continued)

OBSERVATION	Y VALUE	Y ESTIMATE	RESIDUAL	-2SD	0.0	+2SD
158.	3.740000	4.794777	-1.054777		I	
159.	2.870000	3.938964	-1.068964		I	
160.	4.000000	4.209270	-.209270		I	
161.	2.950000	3.802801	-.852801		I	
162.	3.200000	3.075512	.124488		I	
163.	3.810000	4.070873	-.260873		I	
164.	5.780000	4.869786	.910213		I	
165.	4.430000	4.334452	.9554792E-01		I	
166.	3.960000	3.824264	.1357356		I	
167.	3.760000	3.443896	.3161039		I	
168.	3.040000	3.165441	-.1254415		I	
169.	CASE DELETED DUE TO MISSING DATA.					
170.	2.380000	2.686734	-.3067335		I	
171.	2.170000	2.496411	-.3264109		I	
172.	2.310000	2.553234	-.2432340		I	
173.	3.200000	3.014858	.1851421		I	
174.	2.960000	2.653387	.3066132		I	
175.	3.400000	2.857490	.5425102		I	
176.	3.480000	2.672401	.8075988		I	
177.	2.530000	2.420199	.1098009		I	
178.	3.340000	2.846156	.4938440		I	
179.	2.250000	2.374059	-.1240585		I	
180.	2.200000	2.370462	-.1704623		I	
181.	3.920000	3.027980	.8920197		I	
182.	2.450000	2.933621	-.4836211		I	
183.	2.550000	1.964207	.5857931		I	
184.	2.670000	2.415306	.2546941		I	
185.	2.330000	2.577806	-.2478063		I	
186.	2.050000	2.808162	-.7581619		I	
187.	2.290000	2.482129	-.1921288		I	
188.	2.680000	2.905943	-.2259430		I	
189.	1.990000	2.353202	-.3632019		I	
190.	2.160000	2.976438	-.8164379		I	
191.	3.240000	3.560908	-.3209083		I	
192.	1.670000	2.474458	-.8044583		I	
193.	1.930000	2.196096	-.2660975		I	
194.	2.200000	2.398643	-.1986432		I	
195.	2.000000	2.652657	-.6526573		I	
196.	2.400000	2.415651	-.1565112E-01		I	
197.	3.100000	2.549744	.5502561		I	
198.	3.960000	2.782813	1.177187		I	
199.	3.550000	2.770697	.7793027		I	
200.	2.540000	2.657733	-.1177327		I	
201.	CASE DELETED DUE TO MISSING DATA.					
202.	3.530000	3.054530	.4754699		I	
203.	CASE DELETED DUE TO MISSING DATA.					
204.	CASE DELETED DUE TO MISSING DATA.					
205.	3.880000	3.205342	.6746585		I	
206.	3.610000	3.407024	.2029763		I	
207.	4.760000	4.172291	.5877086		I	
208.	4.470000	4.132208	.3377919		I	
209.	CASE DELETED DUE TO MISSING DATA.					

a. Case 106 - 1/4/79 to 1/11/79, Case 209 - 12/30/80 to 1/6/81.

obtaining this by chance was only 0.00004) (155, 166). The pattern of the residuals for Model I suggested the possible influence of seasonal meteorological factors, such as temperature, windspeed, wind direction, dispersion, etc. Correlations between the residuals of the model and other variables in the data set including several functions of temperature, windspeed, 7 A.M. mixing height, and the product of the latter two, were examined. Significant correlations between the residuals and RSPCYC ($r = 0.72$) and an exponential function of temperature (discussed below) were observed. The form of the exponential function was based on the equations of Yamasaki *et al.* (47) which describe the changes in the distribution of PAH between vapor and particulate phases as a function of temperature.

Changes in the ambient temperature over the seasons have been shown to affect the distribution of airborne organic species between the vapor and particulate phases (47) and consequently would be expected to influence the measurement of RSPCYC. During the colder winter months, a greater proportion of the cyclohexane-soluble organics would be expected to condense upon or be adsorbed upon the particles. Similarly, if the surface area of the ambient aerosol increases, a greater proportion of organic matter should be found in the particles (167, 168). Because of the relationships between oil-burning and emissions of vanadium in winter and lower winter temperatures, shifts in the vapor-particle

distribution are probably partially accounted for through the RV term of the model.

An attempt was made to estimate the effect of variations in temperature and aerosol surface area on the measured RSPCYC which might contribute to the unattributed fraction, R, of RSPCYC. The long-term average temperature for New York City, 54.5°F, was chosen as a reference temperature. Since measurements of the surface area of the aerosol for NYC were not available, this was assumed to be proportional to the RSP concentration and the average concentration of RSP, 31.8 µg/m³, was chosen as a standard or reference. The reference state (temperature = 54.5°C and RSP = 31.8 µg/m³) is designated with a "2" in parentheses or as a subscript.

If f_1 = the fraction of RSPCYC in the particulate phase as measured (state "1") and f_2 is the fraction in the reference state (state "2"), then

$$\text{RSPCYC}(2) = \text{RSPCYC}(1) \times \frac{f_2}{f_1}. \quad (4)$$

Define

$$D = \text{RSPCYC}(2) - \text{RSPCYC}(1), \quad (5)$$

and assume that R is proportional to D,

$$R = d \cdot D + R^1 \quad (6)$$

where d is some constant and R^1 is the new remainder.

Then

$$D = \text{RSPCYC}(2) \left[\frac{f_2}{f_1} - 1 \right] \quad (7)$$

According to Junge (167), for the ambient aerosol,

$$f = \frac{k\theta}{P_0 + k\theta} \quad (8)$$

where k = a constant,

θ = the surface area of the aerosol,

P_0 = the saturation vapor pressure of the compound.

Substituting eqn. (8) into eqn. (7) gives:

$$D = \text{RSPCYC}(1) \left[\frac{\theta_2}{\theta_1} \left(\frac{P_1 + k\theta_1}{P_2 + k\theta_2} \right) - 1 \right] \quad (9)$$

where θ_1 , and θ_2 refer to the aerosol surface area under measured and standard conditions, respectively, and P_1 and P_2 refer to the saturation vapor pressures at T_1 and T_2 . In this instance, it is assumed that

$$\frac{\theta_2}{\theta_1} = \frac{\text{RSP}_2}{\text{RSP}_1} = \frac{31.8 \mu\text{g}/\text{m}^3}{\text{RSP}_1} \quad (10)$$

The term $k\theta$ is estimated to be one-to-two orders of magnitude lower than P_1 or P_2 . According to Junge (167), $k \approx 0.13$ cm-torr for many compounds. The value of θ , the surface area of the aerosol per cm^3 has been given as 10^{-7} - 10^{-6} cm^2/cm^3 (167, 168). Corn et al. (169) have measured the surface area of aerosols collected in an urban area, Pittsburgh, and reported values ranging from about 1-4 m^2/g . aerosol. For an RSP concentration of 32 $\mu\text{g}/\text{m}^3$, the equivalent surface area would

be 0.3×10^{-6} to 1.3×10^{-6} cm^2/cm^3 . Consequently $k\theta$ would be expected to range from 0.4×10^{-7} to 1.7×10^{-7} torr. Values of P_0 for anthracene, a compound in the molecular weight range of interest range from 1.2×10^{-5} torr at 270°K to 2.8×10^{-4} torr at 300°K (170). Since $P_0 > k\theta$, eqn (9) was approximated as

$$D = \text{RSPCYC}(1) \left[\frac{31.8}{\text{RSP}_1} \times \frac{P_1}{P_2} - 1 \right] \quad (11)$$

Assuming that the Clausius-Clapeyron equation adequately describes the variation in vapor pressure with temperature,

$$\frac{P_1}{P_2} = e^{-\frac{\Delta H}{2.3R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)} \quad (12)$$

where ΔH is the enthalpy of sublimation.

Therefore,

$$D = \text{RSPCYC}(1) \left[\left(\frac{31.8}{\text{RSP}_1} \right) e^{-\frac{\Delta H}{2.3R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)} - 1 \right] \quad (13)$$

A multiple regression analysis was used to determine the coefficient d of eqn. (6). Equation (13) was used to estimate the values of D . The value of ΔH (heat of sublimation) was assumed to have an average value of 20, 25 or 30 kcal/mole. The selection of a numerical value for ΔH was based on the values reported for those PAH compounds for which the greatest temperature effect on the vapor-particle distribution was observed (47), i.e., chrysene and pyrene. Thus, it was

assumed that the greatest change in the mass of the RSPCYC fraction would be due to compounds with heats of sublimation in this range. The coefficients and residuals for eqn. (6), using different values of ΔH , are presented in Table 5-9. The values of r^2 were very low and F values were marginally significant. The overall remainder, R^1 , did not change significantly, and the time-sequence pattern of the residuals was unchanged. The coefficients for D were statistically significant at only the 0.07 and 0.09 level and this term accounted for only $0.05 \mu\text{g}/\text{m}^3$, about 4% of the remainder of RSPCYC Model I. Although this is only a first order approximation, the effects of variations in temperature and aerosol surface area appear to account for only a small portion of the unattributed RSPCYC and of the RSPCYC mass on an annual basis. In addition, it suggests that inclusion of a variable such as RV in a multiple regression model, which varies seasonally with temperature, automatically provides some compensation for such effects.

These results and the magnitude of the remainder in comparison to the average background concentrations measured for this fraction, suggest that the unattributed RSPCYC of the model is due to contributions from unidentified sources and/or sources upwind of New York City.

5.3.3 Multiple Regression Source Apportionment Model for RSPDCM

The RSPDCM fraction is the smallest in mass of the three organic fractions, usually 10-20% of the total EOM. Infrared spectra indicate the presence of oxidized hydrocarbons in this fraction while mass

Table 5-9. Regression Equations^a. Relating to R of RSPCYC
Model I to Variations in Ambient Temperature and Aerosol
Surface Area

Value of ΔH , kcal/mole	Average Value of $D, \mu\text{g}/\text{m}^3$	Coefficient of $D \pm \text{S.E.}$	R^1	Statistical Measures of goodness of fit		
				r^2	F	p
-20.0	1.11 ± 3.13	0.039 ± 0.022	1.13	0.033	1.97	(0.088)
-25.0	1.65 ± 4.55	0.028 ± 0.016	1.13	0.035	3.17	(0.078)
-30.0	2.35 ± 6.44	0.020 ± 0.011	1.12	0.037	3.36	(0.070)

a. For eqn. (6): $R = d \cdot D + R^1$.

spectral measurements have shown carboxylic acids to be present (171). This fraction was most highly correlated with tracers for resuspended soil, RTI ($r = 0.41$), RFE ($r = 0.34$), RSPMN ($r = 0.26$), and with RS ($r = 0.27$). Since carboxylic acids in ambient aerosol frequently originate from plant waxes and pollen (30, 172), the presence of plant detritus in soil could account for the correlations with the tracers for resuspended soil. These compounds might also be produced in soil by microorganisms (172). The correlation with RS suggests that some of the RSPDCM may be formed through photochemical oxidation of gaseous organics followed by gas-to-particle conversions. Correlations of RSPDCM with sulfate and O_3 have been observed previously (8, 173) and are consistent with such an origin.

The model developed for RSPDCM is shown in Table 5-10. Statistically significant coefficients were obtained for both RTI ($p < 0.001$) and RS ($p = 0.052$). Unfortunately source composition data are lacking for this fraction and the coefficients cannot be verified in this way. The only measurements available for this fraction are on the Allegheny Tunnel samples. The DCM-soluble organics in these samples were only 15% of the CYC-soluble organics. Consequently, motor vehicles would be expected to contribute little to this fraction, as is implied by the model.

Although the value of F was fairly high, the overall r^2 for this model was only 0.23, i.e., it accounts for only 23% of the variance. Filter sampling artifacts may contribute to the lower value of r^2 for

Table 5-10. Multiple Regression Model for RSPDCM^a.

	<u>RTI</u>	Tracers <u>RS</u>	<u>R</u>
Coefficients $\pm$ S.E. ^b	54.6 $\pm$ 13.1	0.112 $\pm$ 0.057	0.28 $\pm$ 0.29
Contributions of Sources:			
$\mu\text{g}/\text{m}^3$	0.92 $\pm$ 0.22	0.44 $\pm$ 0.22	0.28 $\pm$ 0.29
%	56 $\pm$ 13	27 $\pm$ 14	17 $\pm$ 17
Source:	Resuspended soil	Sulfate-related	Residual

a. $n = 90$; overall $r^2 = 0.23$; overall $F = 12.7$ ($p < 0.001$).

b. Coefficients for variables expressed in $\mu\text{g}/\text{m}^3$.

this model. The work of Schwartz et al. (165) suggests that this fraction may be the most highly affected by sampling artifacts. During the winter, 1982 ATEOS sampling campaign, it was observed that the concentration of this fraction determined from samples of fine ($D_{50} \leq 2.5 \mu m$) particulate matter was frequently higher than that determined from samples of inhalable ($D_{50} \leq 15 \mu m$) particulate matter at low concentrations (unpublished data). The distribution of the RSPDCM data from N.Y.C., shown in Figure 5-1, showed some deviation from normality at the lower concentrations which were near the lower limit of detection of this variable. Uncertainties in the measured concentrations would also result in a lowered value of r^2 for the model.

5.3.4 Multiple Regression Source Apportionment Model for RSPACE

The acetone-soluble fraction is the largest of the three organic fractions and has been found to contain oxidized hydrocarbons (171, 173), alkylating agents (13) and some inorganic materials such as nitrate (157). Recent work during ATEOS has shown that during summertime photochemical smog episodes characterized by high levels of sulfate and ozone, the concentration of the ACE fractions increases due to the formation of secondary organic aerosol (157).

In New York City during 1979 and 1980, the RSPACE fraction was most highly correlated with tracers relating to oil-burning-RV ($R = 0.43$), RSPV ($r = 0.47$), RP ($r = 0.52$), and sulfate-RS ($r = 0.34$); all correlations were significant at the $p = 0.001$ level. There was also some correlation with tracers for incineration - RSPCU ($r = 0.17$,

$p = 0.06$) and soil resuspension - RFE ($r = 0.21$, $p = 0.03$),
RTI ($r = 0.20$, $p = 0.026$). A model of the form

$$\text{RSPACE} = a\text{RV} + b\text{RS} + c\text{RSPCU} + d\text{RTI} + R \quad (14)$$

was developed. Although motor vehicles were identified as being a significant source of this fraction in the model developed previously using the 1978 (and part of 1979) data, with the 1979-1980 data, the coefficient for RPB (or RSPPB) was always non-significant and negative. The coefficients and source contributions for the model of eqn. (14) are presented in Table 5-11.

Substituting the variables RFE for RTI or RSPSO4 for RS changes the estimates of the source contributions by only a few percent but the coefficients for these variables were slightly less significant statistically. Coefficients obtained using dispersion normalized data were very similar to those obtained with the ambient data but there was greater multicollinearity between the variables, as evidenced by the lower tolerances obtained for each of the remaining variables in the stepwise fitting. Because of the greater number of samples for the combined 1979 and 1980 period a greater number of coefficients could be obtained for this model than the one developed previously (8).

Comparisons of the coefficients with source emissions data are not currently possible due to the lack of such data. Some comparisons can be made with the 1978-79 model. The coefficient for vanadium in the first model was 19 ± 8 compared to the value of 29 ± 6 obtained for 1979-1980. The coefficient for RSPCU in the first model, 12 ± 19 , was

Table 5-11. Multiple Regression Model for RSPACE^a.

	<u>RV</u>	<u>RS</u>	Tracers <u>RSPCU</u>	<u>RTI</u>	<u>R</u>
Coefficients $\pm$ S.E. ^b	29.4 $\pm$ 6.2	0.28 $\pm$ 0.10	21.7 $\pm$ 10.0	42 $\pm$ 24	1.36 $\pm$ 0.63
Significance	<0.001	0.01	0.033	0.085	0.034
Source Contributions					
$\mu\text{g}/\text{m}^3$	1.26 $\pm$ 0.27	1.08 $\pm$ 0.39	0.54 $\pm$ 0.25	0.71 $\pm$ 0.4	1.36 $\pm$ 0.63
%	26 $\pm$ 5	22 $\pm$ 8	11 $\pm$ 5	14 $\pm$ 6	28 $\pm$ 13
Source Type	Oil-burning	Sulfate-related	Incineration	Resuspended Soil	

a. n = 91 cases; overall F = 10.4 (p<0.001); $r^2 = 0.326$.

b. Coefficients for variables expressed in units of $\mu\text{g}/\text{m}^3$.

not statistically significant but was in reasonable agreement with the coefficient for the current model, 22 ± 10 . Comparisons cannot be made for resuspended soil as coarse particle manganese was used as the tracer for this source in the first model due to the correlation between RSP lead and RSP manganese during this earlier period. The source contributions estimated with the early model (8) and the 1979-1980 model, presented in Table 5-12, are in good agreement for oil-burning and resuspended soil.

In contrast to the model for RSPCYC, the residuals for the RSPACE were more normally distributed, i.e., the expected and actual number of runs of signs were almost identical (46 and 48, respectively). As with the RSPCYC, the unattributed RSPACE may be due in large part to contributions to this fraction from the sites upwind of New York City and to a regional background. Concentrations of RSPACE at the background rural site in Tuxedo, N.Y. averaged $1.6 \mu\text{g}/\text{m}^3$ and ranged from 0.2 to $2.4 \mu\text{g}/\text{m}^3$ during the period, compared to a value of $1.4 \mu\text{g}/\text{m}^3$ for R in the model. Contributions from urban sites to the west of New York City would probably also be in the range, based on the ATEOS Study (13).

5.4 SUMMARY AND CONCLUSIONS

The estimated contributions of each of the identified sources to each of the three EOM fractions and to total EOM, based on the developed models, are summarized in Table 5-13. Residual oil burning accounted for the largest percentage of total EOM among the identified sources, followed by resuspended soil. Motor vehicles accounted for only 6% of the total. It should be kept

Table 5-12. Comparison of Source Contributions of the 1979-1980 Data Model and of the 1978-1979 Data Model for RSPACE

<u>Model</u>	<u>Oil-burning</u>	$\mu\text{g}/\text{m}^3$ (% of Total)		<u>R</u>
		<u>Resuspended Soil</u>	<u>Motor Vehicles</u>	
1978-1979 ^a	1.0(22.8%)	0.97(21.4%)	1.64(36%)	0.90(19.8%)
1979, 1980	1.3(26%)	0.71(14%)	-	1.36(28%)

a. Data for 1979 available for only January through July, 1979.

Table 5-13. Summary of Estimated Contributions of Various Sources to the Average Ambient Concentrations of EOM in New York City for the Years 1979 and 1980.

<u>Source Type</u>	<u>RSPCYC</u>	$\frac{\mu\text{g}}{\text{m}^3}$ <u>RSPDCM</u>	<u>RSPACE</u>	<u>Total EOM</u>
Residual Oil	1.06±0.13	-	1.26±0.27	2.3 ±0.4 (24%)
Motor Vehicles	0.55±0.21	-	-	0.55±0.21 (6%)
Resuspended Soil	0.33±0.20	0.92±0.22	0.71±0.41	2.0 ±0.8 (21%)
Incineration	-	-	0.54±0.25	0.54±0.25 (6%)
Sulfate-Related	-	0.44±0.22	1.08±0.39	1.5 ±0.6 (15%)
Unattributed	1.17±0.33	0.28±0.29	1.36±0.63	2.8 ±1.2 (29%)

in mind that the sampling station is located on top of a 15 story building and thus should be more strongly influenced by rooftop than street level sources. Sulfate-related EOM, which is probably due largely to secondary organic aerosol, accounts for 15% of the total and is found in those fractions in which it would be expected, i.e., the more polar DCM and ACE fractions which contain oxidized hydrocarbons.

The models indicate that the sources of organic aerosol can be different for fractions of differing chemical composition. Twenty-nine percent of the total EOM could not be attributed to known sources but is suspected to originate, in part, from upwind urban regional background sources. Other unidentified sources may contribute to this remainder, as well. The possible influence of filter sampling artifacts on R must also be considered. The samples used for model development were collected over periods of one week in order to maintain continuity with TSP sampling begun in 1967. For organic sampling, 12 or 24 hr. samples would be more appropriate as volatilization losses and filter reactions would be minimized.

This work has demonstrated the feasibility of developing receptor source apportionment models for particulate organic matter and has also identified some of the critical problems to be solved for further development such as model validation, the need for simultaneous measurements of background organic aerosol, and the need for appropriate tracers for such background aerosol. The coefficients of the source tracers in the models were in quite satisfactory agreement with available source emissions data, supporting the validity of the models. However, the lack of organic composition data for

source emissions is a critical limitation for both model validation and for model development in the case of chemical mass balance models.

SECTION 6

PHILADELPHIA STUDY

6.1 INTRODUCTION

As part of the Philadelphia Model Evaluations Study of 1982, samples of inhalable ($D_{50} \leq 15 \mu m$) particulate matter were collected for organic analyses during the summer of 1982. Samples were analyzed for three fractions of extractable organic matter (EOM) and the non-polar (cyclohexane-soluble) organic fraction was analyzed for polycyclic aromatic hydrocarbons (PAH). The purpose of this work was to provide some information on concentrations of particulate organic species during the Philadelphia study, and, if possible, to use these data for further development of receptor models.

6.2 EXPERIMENTAL

6.2.1 Site Description

Samples were collected at the Fireboat Station, located on the Delaware River, at the intersection of Delaware and Allegheny Streets in Philadelphia, PA. The location of the station is shown in Figure 6-1. The location of the New Jersey ATEOS* (13) sampling station in Camden, N.J., to the south-southwest, is also indicated in the figure. Samples were being collected simultaneously at the Camden site as part of the ATEOS program (13). Figure 6-2 is a diagram of the position of the sampler relative to the river and to major traffic arteries in the immediate area. The area to the west of the Delaware River and the sampler is largely residential. Interstate Highway 95 is about 2 blocks to the west of the station and is a heavily travelled road. During

*ATEOS - Airborne Toxic Elements and Organic Substances - a research program supported by the State of New Jersey and operated by New York University Medical Center.

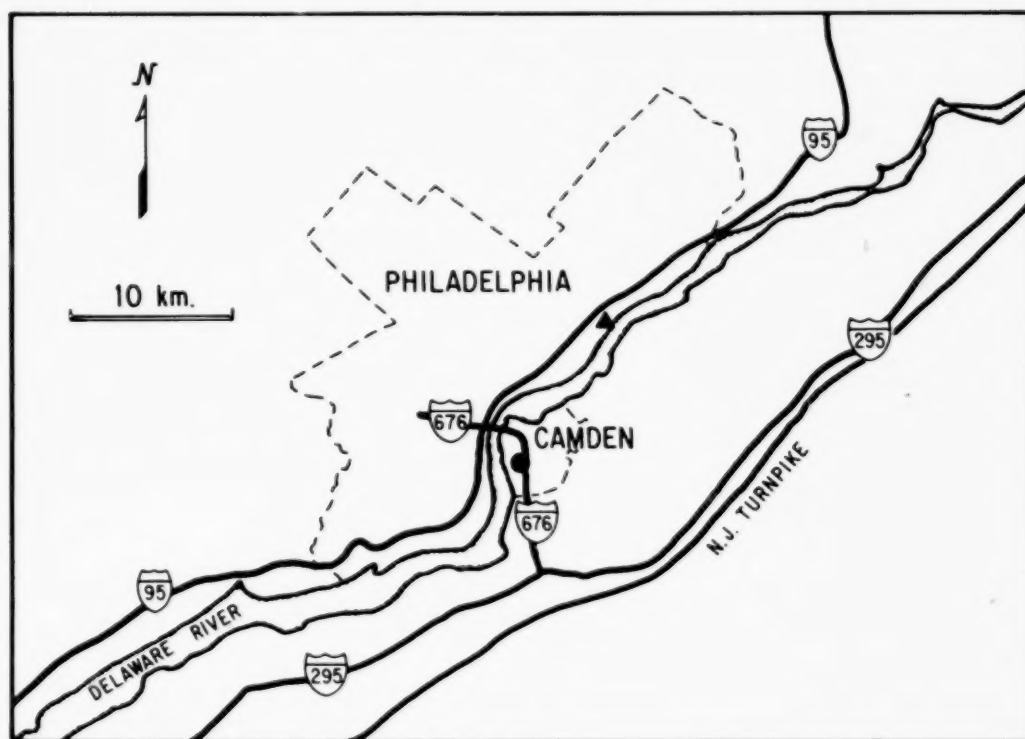


Figure 6-1. Location of Philadelphia Fireboat Sampling Station (▲) and ATEOS Camden Sampling Station (●).

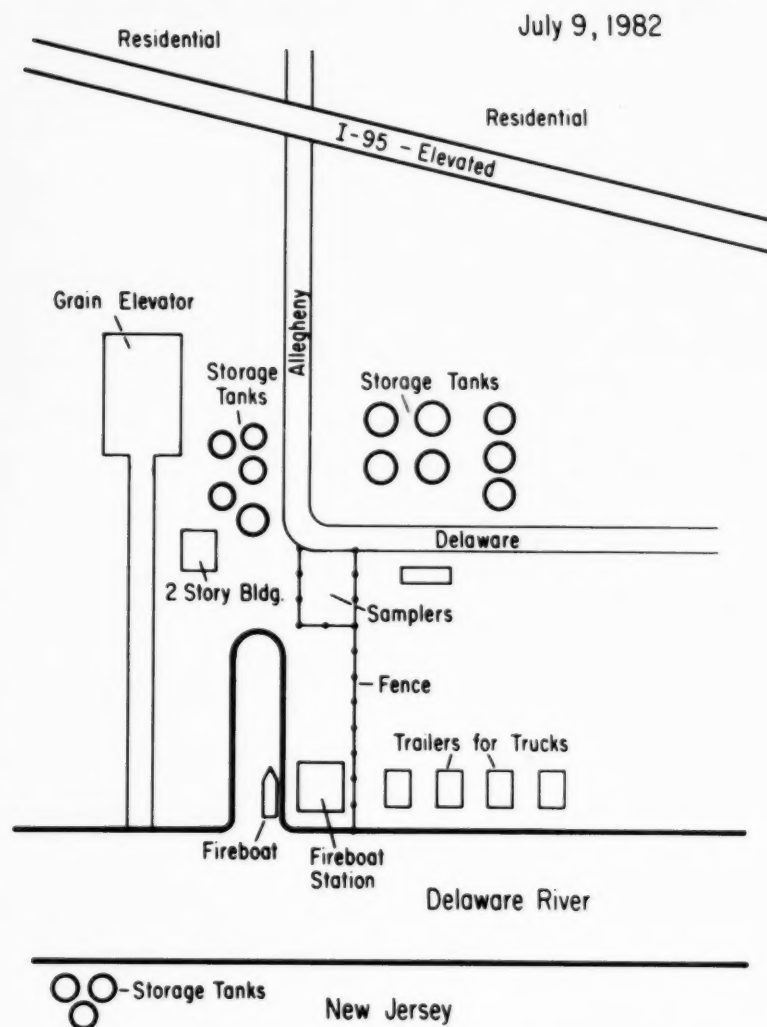


Figure 6-2. Schematic diagram of sampler location relative to the Delaware River and major traffic arteries in the area.

midweek, when the sampler was calibrated, a great deal of diesel truck traffic was observed on Allegheny and Delaware Streets, i.e., about one truck every few minutes. Storage tanks were located in the immediate vicinity of the sampler and also to the southwest of the site, across the river. The storage tanks in the area are used for organic solvent storage and solvent odors could be detected at the site. A grain elevator to the south of the the sampler was not operational during the sampling period.

6.2.2 Sample Collection

Samples of IPM were collected every 24 hrs. from 7/25/82 through 8/14/82 on Gelman Type AE glass fiber filters which had been pre-ignited in a muffle oven at 400°C for 48 hrs. to reduce organic background. The sampler was provided by the Philadelphia Division of Air Management and calibrated by New York University Medical Center personnel. PEDCO personnel collected the samples daily and transferred them to the ATEOS sampling site at the Institute of Medical Research in Camden. The transfers were made at intervals for shipment to the NYU Laboratories in Tuxedo, N.Y. along with the ATEOS samples. The samples were stored in a freezer and shipped with cold packs (0°C). Upon receipt at NYU, the samples were stored overnight in a freezer at -30°C. Organic extractions were initiated within 24 hours of receipt of the samples.

Although PEDCO personnel had been instructed, verbally and in writing, on the protocols for sample collection, storage and transfer, these protocols were not always followed, particularly during the first

week of sampling. Because of sample mishandling, as well as evidence of a leak around the filter during this period, the first 8 samples were discarded. The leak, due to a mis-aligned gasket, was corrected by 7/25/82.

6.2.3 Sample Extraction and Analyses

Half of each sample was extracted sequentially with cyclohexane (CX), dichloromethane (DCM) and, finally, acetone (ACE). Details are provided in Appendix D. The CX fraction was analyzed for PAH compounds as described in Appendix D. Blank filters were extracted in the same way. All extract weights were blank corrected. Table 6-1 summarizes the data for the filter-solvent blank determined during the same period using solvents of the same lot number. The lower limits of detection, calculated according to the method of Gabriels (174) are also included. The average air volume, 816 m^3 (0.5 of sample), was used in this calculation.

6.2.4 Quality Assurance

The quality assurance practices followed in the NYU Laboratory of Environmental Studies are described in Appendix F.

6.3 RESULTS

The concentrations of extractable organic matter determined for this site from 7/25/82 to 8/14/82 are presented in Table 6-2. Arithmetic and geometric means are included in the Table. Consistent with previous research, concentrations of the ACE fraction were the highest followed in decreasing order by CX and DCM. The data for the ATEOS Camden site, which is located

Table 6-1. Data on 20 Filter-solvent Blanks

Extraction Solvent	Blank Correction, ^a mg ($\pm$ S.D.)	Lower Limit of Detection, ^b $\mu\text{g}/\text{m}^3$
Cyclohexane	0.03 $\pm$ 0.02	0.06
Dichloromethane	0.31 $\pm$ 0.14	0.54
Acetone	0.24 $\pm$ 0.09	0.40

a. Half of 8" x 10" Gelman Type AE filter, pre-ignited at 400°C for 48 hrs, stored in aluminum foil, extracted sequentially with 200 ml of each solvent.

b. Method of Gabriels (174) used to calculate lower limit of detection, with an average air volume of 816 m³.

Table 6-2. Concentrations of Extractable Particulate Organic Matter in Inhalable ($\leq 15 \mu\text{m}$, A.D.) Particulate Matter collected in Philadelphia (Fireboat Station)

Sample No.	Date	Concentrations of Extracts, $\mu\text{g}/\text{m}^3$		
		CX	DCM	ACE
663	7/25-7/26/82	2.8	3.5	12.4
664	7/26-7/27/82	3.5	2.1	14.8
666	7/28-7/29/82	3.8	1.7	8.4
669	7/29-7/30/82	5.8	2.2	8.4
668	7/30-7/31/82	2.5	1.0	7.3
670	7/31-8/ 1/82	2.0	1.3	6.0
671	8/ 1-8/ 2/82	1.7	0.8	9.5
672	8/ 2-8/ 3/82	3.7	1.8	8.2
673	8/ 3-8/ 4/82	4.1	4.0	9.9
674	8/ 4-8/ 5/82	2.8	4.7	12.1
675	8/ 5-8/ 6/82	2.8	3.9	9.9
676	8/ 6-8/ 7/82	1.8	2.0	9.8
677	8/ 7-8/ 8/82	1.1	1.1	3.8
678	8/ 8-8/ 9/82	0.7	1.1	4.1
679	8/ 9-8/10/82	1.7	2.4	4.3
680	8/10-8/11/82	2.4	2.5	10.8
682	8/11-8/12/82	2.1	1.6	2.8
684	8/13-8/14/82	3.7	1.9	6.9
Mean $\pm$ S.D.		: 2.7 $\pm$ 1.2	2.2 $\pm$ 1.1	8.3 $\pm$ 3.3
Geometric mean		: 2.4	1.9	7.6
og		: 1.7	1.7	1.6

across the Delaware River and to the south of the Philadelphia site, are available for comparison and the geometric mean for each fraction is shown in Table 6-3. The means of the Camden samples are for the same sampling period. The Philadelphia samples were higher in the non-polar (CX) and moderately polar (DCM) fractions, while the Camden samples were higher in the polar (ACE) fraction.

Daily variations in the concentrations of these three EOM fractions are shown in Figure 6-3. Similar measurements made at the Camden ATEOS site are shown in Figure 6-4 for comparison. Some intersite correlation is apparent for all three fractions, presumably due to the proximity of the sites. The highest intersite correlation ($r = 0.70$, $p = 0.01$) was observed for the polar ACE fraction. Concentrations of ACE reached peak levels at both sites on 7/26, 8/10 and between 8/2 and 8/6/82. Previous studies in New Jersey have shown that during the summer the ACE fraction is frequently highly correlated with sulfate concentrations (13, 157). During summertime episodes of elevated concentration of IPM , $\text{SO}_4^{=}$ and O_3 , secondary organic aerosol formation contributes to the ambient levels of the ACE fraction and this additional secondary aerosol appears to be distributed over the region (157). During such periods, intersite correlations would tend to increase for the ACE fraction.

The variations in concentrations also suggest a weekday-weekend differences, particulatly for the CX fraction. The dates 7/25 (Sunday), 7/31 and 8/1, 8/7 and 8/8 fell on weekends and concentration minima were observed at the Philadelphia site on all three weekends in the case of the CX fraction

Table 6-3. Comparison of Mean Concentrations of Extractable Particulate Organic Matter at the Philadelphia Site and the ATEOS Camden Site

<u>Site</u>	Geometric Mean (σ), $\mu\text{g}/\text{m}^3$		
	<u>CX</u>	<u>DCM</u>	<u>ACE</u>
Philadelphia	2.4 (1.7)	1.9 (1.7)	7.8 (1.6)
Camden	2.0 (1.5)	1.5 (1.5)	8.2 (1.5)

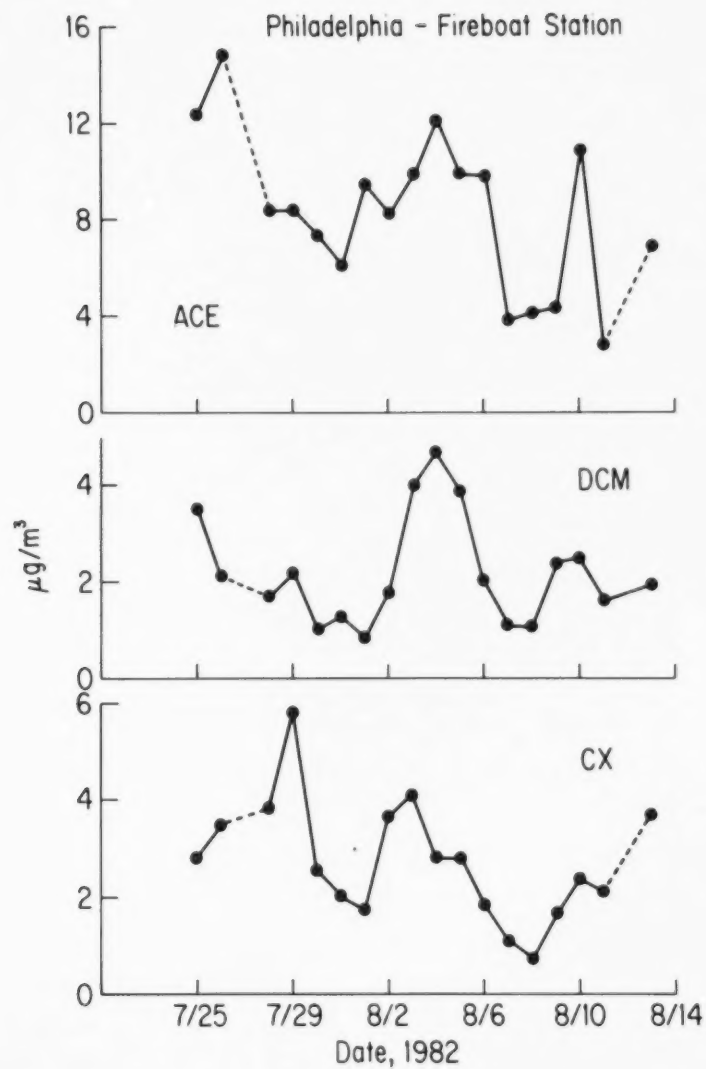


Figure 6-3. Variations in concentrations of cyclohexane (CX)-, dichloromethane (DCM)-, and acetone (ACE)-soluble organic matter at the Philadelphia Fireboat Station.

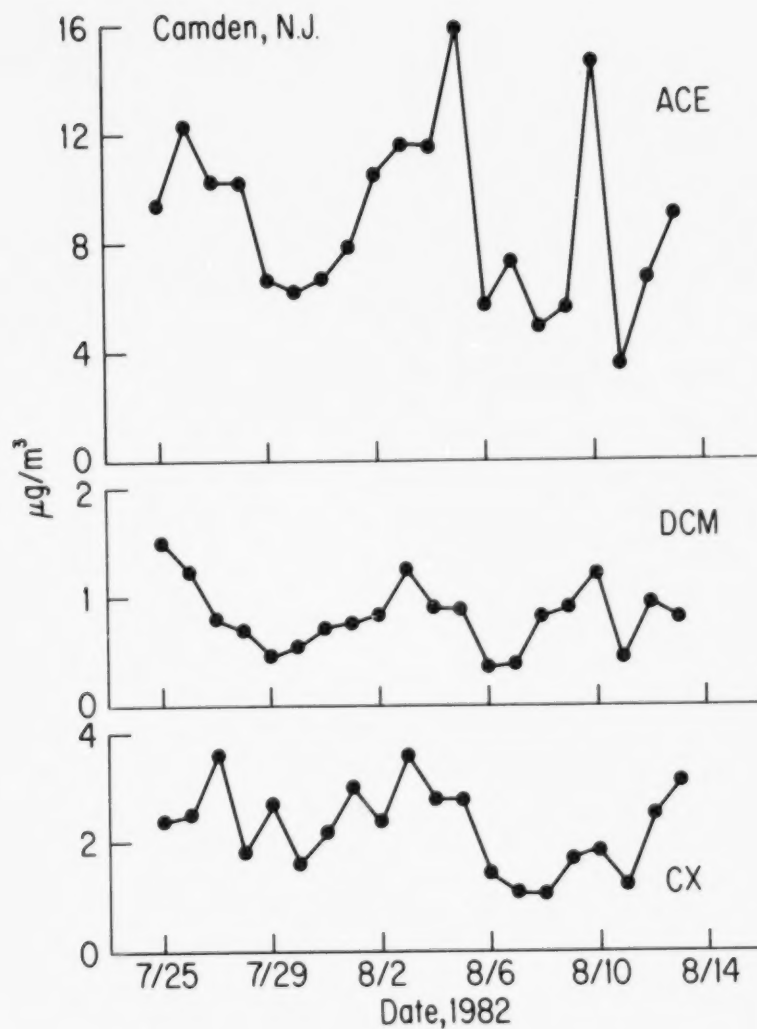


Figure 6-4. Variations in concentrations of cyclohexane (CX)-, dichloromethane (DCM)-, and acetone (ACE)-soluble organic matter at the Camden ATEOS Station.

and on the latter two weekends for the DCM and ACE fractions (Figure 4-3). Less diesel traffic at this site on the weekends may account for the lower concentrations of CX in particular. The CX fraction contains non-polar aliphatic, aromatic and polycyclic aromatic hydrocarbons which in urban areas are generally directly emitted by combustion sources (14, 19), i.e., primary aerosol. Emissions from diesel engines have a very high proportion of aliphatic hydrocarbons (41, 90).

The atmospheric concentrations of 12 PAH compounds determined during the period of this study are presented in Table 6-4. Concentrations were generally less than 1 ng/m^3 . Peak PAH concentrations, observed on 7/29 and 8/2, coincided with elevated concentrations of the CX fraction. Average concentrations of all of the PAH compounds were lower on the weekends than on the weekdays, as shown in Table 6-5, suggesting that motor vehicle traffic was the major source of the PAH during this period as might be expected.

Comparisons have not been made between the PAH profiles of the Philadelphia samples and those of motor vehicle or tunnel samples for two reasons. The chief reason is the inadequacy of existing source profiles for this purpose, as discussed in Section 4. Photochemical and filter reactions of the PAH during summertime sampling periods can be expected to alter the source profiles in ways which cannot yet be predicted, thus the adequacy of any profiles would be suspect for summertime conditions.

Table 6-4. Atmospheric Concentrations of PAH at the Philadelphia Fireboat Station, Summer 1982, ng/m³

Compound	DATE (Day of Week)									
	7/25(Su)	7/26(M)	7/28(W)	7/29(Th)	7/30(F)	7/31(Sa)	8/1(Su)	8/2(M)	8/3(Tu)	
Fluoranthene	0.40	1.18	0.89	1.99	0.35	0.32	0.33	1.36	1.11	
Pyrene	0.23	0.82	0.66	1.58	0.25	0.22	0.26	0.18	0.79	
Benz(a)anthracene	0.10	0.40	0.29	1.02	0.10	0.07	0.07	0.50	0.41	
Chrysene	0.48	2.06	0.83	2.76	0.39	0.38	0.79	4.35	1.68	
Benzo(b)fluoranthene	0.09	0.69	0.45	1.12	0.12	0.23	0.10	0.74	0.53	
Benzo(k)fluoranthene	0.04	0.48	0.10	0.99	0.08	0.13	0.06	1.10	0.25	
Benzo(j)fluoranthene	0.22	0.78	0.53	0.93	0.21	0.36	0.20	1.06	0.58	
Benzo(e)pyrene	0.28	0.88	1.24	2.39	0.54	0.42	0.27	2.61	1.28	
Benzo(a)pyrene	0.06	0.44	0.29	1.11	0.10	0.11	0.04	0.61	0.41	
Perylene	<0.002	0.08	0.07	0.20	0.002	0.006	0.006	0.17	0.10	
Benzo(ghi)perylene	0.07	0.68	0.74	1.48	0.17	0.37	0.28	1.05	0.77	
Indeno(1,2,3-cd)pyrene	0.3	0.45	0.31	0.98	0.08	0.19	0.05	0.61	0.38	
Total	2.27	8.94	6.40	16.55	2.39	2.81	2.46	14.34	8.29	

Table 6-4. Atmospheric Concentrations of PAH at the Philadelphia Fireboat Station, Summer 1982, ng/m³
(continued)

Compound	DATE (Day of Week)								
	8/4(W)	8/5(Th)	8/6(F)	8/7(Sa)	8/8(Su)	8/9(M)	8/10(Tu)	8/11(W)	8/13(F)
Fluoranthene	0.33	0.33	0.19	0.14	0.06	0.13	0.34	0.36	1.06
Pyrene	0.22	0.18	0.25	0.10	0.01	0.09	0.24	0.36	0.76
Benz(a)anthracene	0.04	0.05	0.14	<0.02	<0.02	0.02	0.05	0.14	1.36
Chrysene	0.64	0.56	0.43	<0.10	<0.10	<0.10	0.10	0.08	0.29
Benzo(b)fluoranthene	0.07	0.13	0.15	0.06	<0.05	0.05	0.16	0.16	0.78
Benzo(k)fluoranthene	0.09	0.07	0.14	<0.04	<0.04	0.06	0.11	0.12	0.07
Benzo(j)fluoranthene	0.18	0.18	0.21	0.12	<0.10	0.23	0.17	0.29	1.12
Benzo(e)pyrene	0.30	0.42	0.63	<0.006	0.006	0.29	0.49	0.78	1.90
Benzo(a)pyrene	0.03	0.05	0.12	<0.03	<0.03	0.13	0.11	0.24	1.07
Perylene	<0.002	<0.002	0.02	<0.002	<0.002	<0.002	<0.002	0.002	0.19
Benzo(ghi)perylene	0.19	0.08	0.22	<0.07	<0.07	0.15	0.24	0.53	1.84
Indeno*1,2,3-cd)pyrene	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.09	0.14	1.05
Total ^a .	2.11	2.07	2.52	0.57	0.35	1.22	2.10	3.20	11.49

a. One-half the detection limit used for values below this limit.

Table 6-5. Average (1 S.D.)^a. Weekday and Weekend Concentrations of PAH Compounds, ng/m³

<u>Compound</u>	<u>Weekdays</u>	<u>Weekends</u>
Fluoranthene	0.74±0.57	0.25 ±0.14
Pyrene	0.57±0.45	0.16 ±0.11
Benz(a)anthracene	0.35±0.41	0.05 ±0.04
Chrysene	1.09±1.29	0.35 ±0.31
Benzo(b)fluoranthene	0.40±0.35	0.10 ±0.08
Benzo(k)fluoranthene	0.28±0.36	0.05 ±0.05
Benzo(j)fluoranthene	0.50±0.36	0.19 ±0.12
Benzo(e)pyrene	0.16±0.79	0.20 ±0.18
Benzo(a)pyrene	0.36±0.37	0.06 ±0.04
Perylene	0.06±0.08	0.003±0.003
Benzo(ghi)perylene	0.63±0.55	0.16 ±0.16
Indeno(1,2,3-cd)pyrene	0.32±0.36	0.06 ±0.07
Mean of Total PAH	6.28±5.21	1.69 ±1.14

a. n = 13 for weekdays; n = 5 for weekends; in calculating the average concentrations, one-half the detection limit was used for values less than the detection limit.

REFERENCES

1. Friedlander, S. K. Chemical Element Balances and Identification of Air Pollution Sources. Environ. Sci. Technol., 7: 235-240, 1973.
2. Kleinman, M. T., B. S. Pasternack, M. Eisenbud, and T. J. Kneip. Identifying and Estimating the Relative Importance of Sources of Airborne Particulates. Environ. Sci. Technol., 14: 62-65, 1980.
3. Cooper, J. A., and J. G. Watson, Jr. Receptor Oriented Methods of Air Particulate Source Apportionment. J. Air Pollut. Control Assoc., 30: 1116-1125, 1980.
4. Gordon, G. E. Receptor Models. Environ. Sci. Technol., 14: 792-800, 1980.
5. Kneip, T. J., R. P. Mallon, and M. T. Kleinman. The Impact of Changing Air Quality on Multiple Regression Models for Coarse and Fine Particle Fractions. Atmos. Environ., 17(2): 299-304, 1983.
6. Henry, R. C., C. W. Lewis, P. K. Hopke, and H. J. Williamson. Review of Receptor Model Fundamentals. Atmos. Environ., in press.
7. Daisey, J. M., M. A. Leyko and T. J. Kneip. Source Identification and Allocation of Polynuclear Aromatic Hydrocarbon Compounds in the New York City Aerosol: Methods and Applications. In: Polynuclear Aromatic Hydrocarbons, P. W. Jones and P. Leber, eds., Ann Arbor Science Publishers, Inc., Ann Arbor, MI., 1979, pp. 201-215.
8. Daisey, J. M. and T. J. Kneip. Atmospheric Particulate Organic Matter: Multivariate Models for Identifying Sources and Estimating Their Contributions to the Ambient Aerosol. In: Atmospheric Aerosol: Source/Air Quality Relationships, ACS Symposium Series No. 167, E. S. Mascias and P. K. Hopke, eds., American Chemical Society, Washington, D.C., 1981, pp. 197-221.
9. Friedlander, S. K. New Developments in Receptor Modeling Theory. In: Atmospheric Aerosol, Source/Air Quality Relationships, ACS Symposium Series No. 167, E. S. Mascias and P. K. Hopke, eds., American Chemical Society, Washington, D.C., 1981, pp. 1-19.
10. Shah, J. J., J. Huntzicker, T. J. Kneip and J. M. Daisey. Investigation of the Sources of Carbonaceous Aerosol in New York City by Multiple Linear Regression. Paper No. 81-64.3 presented at the 74th Annual Meeting of the Air Pollution Control Association, Philadelphia, PA., June 21-26, 1981.

11. Shah, J. J. Measurements of Carbonaceous Aerosol Across the U.S.: Sources and Role in Visibility Degradation, Doctoral dissertation, Oregon Graduate Center, 1981.
12. Daisey, J. M. Organic Compounds in Urban Aerosols. Ann. N.Y. Acad. Sci., 338: 50-69, 1980.
13. Liroy, P. J., J. M. Daisey, T. Atherholt, J. Bozzelli, F. Darack, R. Fisher, A. Greenberg, R. Harkov, B. Kebbekus, T. J. Kneip, J. Louis, G. McGarrity, L. McGeorge, and N. M. Reiss. The New Jersey Project on Airborne Toxic Elements and Organic Substances (ATEOS): A Summary of the 1981 Summer and 1982 Winter Studies. J. Air Pollut. Control Assoc., 33(7): 549-657, 1983.
14. National Academy of Sciences. Particulate Polycyclic Organic Matter. Washington, D.C., 1972.
15. Hoffmann, D. and E. L. Wynder. Organic Particulate Pollutants--Chemical Analyses and bioassays for Carcinogenicity. In: Air Pollution, A. C. Stern, ed., 3rd edition, 2, Academic Press, Inc., New York, N.Y., 1977, pp. 361-455.
16. Talcott, R., and E. Wei. Airborne Mutagens Bioassayed in Salmonella Typhimurium. J. Natl. Cancer Inst., 58: 449-451, 1977.
17. Daisey, J. M., T. J. Kneip, I. Hawryluk, and F. Mukai. Seasonal Variations in the Bacterial Mutagenicity of Airborne Particulate Matter in New York City. Environ. Sci. Technol., 14: 1487-1490, 1980.
18. Cooper, J. A. Environmental Impact of Residential Wood Combustion Emissions and Its Implications. J. Air Pollut. Control Assoc., 30: 855-861, 1980.
19. Pierson, W. R., and W. W. Brachaczek. Particulate Matter Associated with Vehicles on the Road. II. Aero. Sci. Technol., 2: 1-14, 1983.
20. Freudenthal, R., and P. W. Jones, eds., Polynuclear Aromatic Hydrocarbons: Chemistry, Metabolism, and Carcinogenesis, Raven Press, N.Y., 1976.
21. Jones, P. W., and R. I. Freudenthal, eds., Polynuclear Aromatic Hydrocarbons: Second International Symposium on Analysis Chemistry, and Biology, Raven Press, N.Y., 1978.

22. Jones, P. W., and P. Leber, eds., Polynuclear Aromatic Hydrocarbons: Third International Symposium on Chemistry and Biology - Carcinogenesis and Mutagenesis, Ann Arbor Science Publishers, Inc., Ann Arbor, MI., 1979.
23. Bjorseth, A., and A. J. Dennis, eds., Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects, Battelle Press, Columbus, OH., 1980.
24. Cooke, M., and A. J. Dennis, eds., Chemical Analysis and Biological Fate: Polynuclear Aromatic Hydrocarbons, Battelle Press, Columbus, OH., 1981.
25. Cooke, M., A. J. Dennis, and G. L. Fisher, eds., Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry, Battelle Press, Columbus, OH., 1982.
26. Cooke, M., and A. J. Dennis, eds., Polynuclear Aromatic Hydrocarbons: Formation, Metabolism and Measurement, Battelle Press, Columbus, OH., 1983.
27. Cooper, J. A., and D. Malek, eds., Residential Solid Fuels, Environmental Impacts and Solutions, Oregon Graduate Center, Beaverton, OR., 1982.
28. Frederick, E. R., ed., Residential Wood and Coal Combustion, Proceeding of an APCA Specialty Conference, SP-45, March 1-2, 1982, Louisville, KY., Air Pollution Control Association, 1982.
29. Lamb, S. I., C. Petrowski, I. R. Kaplan, and B. R. T. Simoneit. Organic Compounds in Urban Atmospheres: A Review of Distribution, Collection and Analysis. J. Air Pollut. Control Assoc., 30: 1098-1115, 1980.
30. Simoneit, B. R. T., and M. A. Mazurek. Air Pollution: The Organic Components. CRC Critical Reviews in Environmental Control, 11: 219-276, 1981.
31. Lamb, S. I., and N. E. Adin. Polar Organic Pollutants in Air: A Review of Collection and Analysis. Environ. Intern., 9: 225-243, 1983.
32. Graedel, T. E. Chemical Compounds in the Atmosphere. Academic Press, New York, 1978.
33. Scientific and Technical Assessment Report on Particulate Polycyclic Organic Matter (PPOM), Assembled by the National Environmental Research Center, Research Triangle Park, N.C., for the U.S. Environmental Protection Agency, Report No. EPA-600/6-74-001, 1975.

34. Cass, G. R., P. M. Boone and E. S. Macias. Emissions and Air Quality Relationships for Atmospheric Carbon Particles in Los Angeles. In: Particulate Carbon, Atmospheric Life Cycle, G. T. Wolff, and R. L. Klimisch, Eds., Plenum Press, New York, 1982, pp. 207-243.
35. Hall, R. E., and D. G. DeAngelis. EPA's Research Program for Controlling Residential Wood Combustion Emissions. J. Air Pollut. Control Assoc., 30: 862-867, 1980.
36. Lipfert, F. W., and J. L. Dungan. Residential Firewood Use in the United States. Science, 219: 1425-1427, 1983.
37. Bridges, E. M. World Soils, Cambridge University Press, Cambridge, England, 1970.
38. Delany, A. c., and S. Zenchelsky. The Organic Component of Wind Erosion Generated Soil Derived Aerosol. Soil Sci., 121 146-155, 1976.
39. Butler, J. D., and P. Crossley. Reactivity of Polycyclic Aromatic Hydrocarbons Adsorbed on Soot Particles. Atmos. Environ., 15: 91-94, 1981.
40. Katz, M., C. Chan, H. Tosine, and T. Sakuma. Relative Rates of Photochemical and Biological Oxidation (in vitro) of Polynuclear Aromatic Hydrocarbons. In: Carcinogenesis: A Comprehensive Survey in Polynuclear Aromatic Hydrocarbons. Third International Symposium, P. W. Jones and P. Leber, eds., Ann Arbor Science Publishers, Inc., Ann Arbor, MI., 1979, pp. 171-189.
41. Informational Report on the Measurement of Diesel Particulate Emissions, Prepared by the Smoke and Particulate Panel of the CRC - Program Group on Composition of Diesel Exhaust, Air Pollution Research Advisory Committee of the Coordinating Research Council, Inc. G. P. Gross, J. S. MacDonald and S. M. Shahed, eds., Atlanta, GA., 1982.
42. Stenberg, U., T. Alsberg, and R. Westerholm. Emission of carcinogenic components with Automobile Exhausts. Environ. Health Pers., 47: 53-61, 1983.
43. Sigsby, J. E., Jr., Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, N.C., Personal Communication.
44. Zelenski, S. G., N. Pangaro, and J. M. Hall-Enos. Inventory of Organic Emissions from Fossil Fuel Combustion for Powr Generation. Report No. EA-1394, TSP 78-820, prepared for the Electric Power Research Institute, Palo alto, CA., April, 1980

45. Thrane, K. E., and A. Mikalsen. High-Volume Sampling of Airborne Polycyclic Aromatic Hydrocarbons Using Glass Fibre Filters and Polyurethane Foam. Atmos. Environ., **15**: 909-918, 1981.
46. Cautreels, W., and K. Van Cauwenberghe. Experiments on the Distribution of Organic Pollutants Between Airborne Particulate Matter and the Corresponding Gas Phase. Atmos. Environ., **12**: 1133-1141, 1978.
47. Yamasaki, H., K. Kuwata, and H. Miyamoto. Effects of Ambient Temperature on Aspects of Airborne Polycyclic Aromatic Hydrocarbons. Environ. Sci. Technol., **16**: 189-194, 1982.
48. Swarin, S. J., and R. L. Williams. Liquid Chromatographic Determination of Benzo(a)pyrene in Diesel Exhaust Particulate: Verification of the Collection and Analytical Methods. In: Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects, A. Bjorseth and A. J. Dennis, eds., Battelle Press, Columbus, OH., 1980, pp. 771-790.
49. Grimmer, G. Analysis of Automobile Exhaust Condensates. In: Air Pollution and Cancer in Man. U. Mohr, D. Schmahl, and L. Tomatis, eds., IARC Scientific Publication No. 16, 1977, pp. 29-39.
50. Gorse, Jr., R. A., T. L. Riley, F. C. Ferris, A. M. Pero, and L. M. Skewes. 1-Nitropyrene Concentration and Bacterial Mutagenicity in On-Road Vehicle Particulate Emissions. Environ. Sci. Technol., **17**: 198-202, 1983.
51. Ross, M. M., T. H. Risby, S. S. Lestz, and R. E. Yaskin. Isosteric Heats of Adsorption of Selected Compounds on Diesel Particulate Matter. Environ. Sci. Technol., **16**: 75-78, 1982.
52. Ross, M. M., T. H. Risby, W. A. Steele, S. S. Lestz, and R. E. Yasbin. Physicochemical Properties of Diesel Particulate Matter. Colloids Surf., **5**: 17-31, 1982.
53. MacDonald, J. S., S. L. Plee, J. B. D'Arcy, and R. M. Schreck. Experimental Measurements of the Independent Effects of Dilution Ratio and Filter Temperature on Diesel Exhaust Particulate Samples. SAE Paper No. 800185, SAE Congr. Exp., 1980.
54. Plee, S. L. and J. S. MacDonald. Some Mechanisms Affecting the Mass of Diesel Exhaust Particulate Following a Dilution Process. Diesel Combust. Emiss., SAE Paper No. 800186, SAE Congr. Exp., 1980.

55. Jones, P. W., R. D. Giammar, P. E. Strup and T. B. Stanford. Efficient Collection of Polycyclic Organic Compounds from Combustion Effluents. Environ. Sci. Technol., **10**: 806-810, 1976.
56. Johnson, L. D., and R. G. Merrill. Stack Sampling for Organic Emissions. Toxicol. Environ. Chem., **6**: 109-126, 1983.
57. Cuffe, S.T. and R. W. Gerstle. Emissions from Coal-Fired Power Plants: A Comprehensive Summary. Public Health Service Publication No. 999-AP-35, 1967.
58. Korfmacher, W. A., G. Mamantov, E. L. Wehry, D. F. S. Natusch, and T. Mauney. Nonphotochemical Decomposition of Fluorene Vapor-Adsorbed on Coal Fly Ash. Environ. Sci. Technol., **15**: 1370-1375, 1981.
59. Taskar, P. K., J. J. Solomon and J. M. Daisey. Rates and Products of Reaction of Pyrene Adsorbed on Carbon, Silica and Alumina. Proceedings of the Eighth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, OH., October 26-28, 1983. in press.
60. Griest, W. H., and J. E. Caton. Studies of the Interaction of Polycyclic Aromatic Hydrocarbons with Fly Ash. In: Chemical Analysis and Biological Fate: Polynuclear Aromatic Hydrocarbons, M. Cooke and A. J. Dennis, eds., Battelle Press, Columbus, OH., 1981, pp. 719-730.
61. Tomkins, B. A., R. R. Reagan, M. P. Maskarinec, S. H. Harmon, W. H. Griest, and J. E. Canton. Analytical Chemistry of Polycyclic Aromatic Hydrocarbons Present in Coal-Fired Power Plant Fly Ash. In: Polynuclear Aromatic Hydrocarbons: Formation, Metabolism and Measurement, M. Cooke and A. J. Dennis, eds., Battelle Press, Columbus, OH, 1983, pp. 1173-1187.
62. Lee, F. S.-C, W. R. Pierson, and J. Ezike. The Problem of PAH Degradation During Filter Collection of Airborne Particulates - An Evaluation of Several Commonly Used Filter Media. In: Polynuclear Aromatic Hydrocarbons: Fourth International Symposium on Analysis, Chemistry and Biology, A. Bjorseth and A. J. Dennis, eds., Battelle Press, Columbus, OH., 1980, pp. 543-563.
63. Peters, J., and B. Seifert. Losses of Benzo(a)pyrene Under the Conditions of High-Volume Sampling. Atmos. Environ., **14**: 117-119, 1980.
64. Cautreels, W., and K. Van Cauwenberghe. Extraction of Organic Compounds from Airborne Particulate Matter. Water, Air, Soil Pollution, **6**: 103-110, 1976.

65. Golden, C., and E. Sawicki. Ultrasonic Extraction of Total Particulate Aromatic Hydrocarbons (Tp AH) from Airborne Particles at room Temperature. Intern. J. Environ. Anal. Chem., 4: 9-23, 1975.
66. Griest, W. H., J. E. Caton, M. R. Guerin, L. B. Yeatts, Jr., and C. E. Higgins. Extraction and Recovery of Polycyclic Aromatic Hydrocarbons from High Sorptive Matrices such as Fly Ash. In: Polynuclear Aromatic Hydrocarbons, Chemistry and Biological Effects, A. Bjorseth and A. J. Dennis, eds., 1980, pp. 819-828.
67. Bjorseth, A., Ed. Handbook of Polycyclic Aromatic Hydrocarbons, Marcel Dekker, Inc., New York, 1983.
68. Sawicki, E. Analysis for Airborne Particulate Hydrocarbons: Their Relative Proportions as Affected by Different Types of Pollution. Natl. Cancer Inst. Monogr., 9: 201-220, 1962.
69. Hangebrauck, R. P., D. J. Von Lehmden, and J. E. Meeker. Sources of Polynuclear Hydrocarbons in the Atmosphere. Public Health Service Publication No. 999-AP-33, Cincinnati, OH., 1967.
70. Bartle, K. D., M. L. Lee and M. Novotny. High-Resolution GLC Profiles of Urban Air Pollutant Polynuclear Aromatic Hydrocarbons. Int. J. Environ. Anal. Chem., 3: 349-356, 1974.
71. Grimmer, G., K.-W. Naujack and D. Schneider. Changes in PAH Profiles in Different Areas of A City During the Year. In: Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects, A. Bjorseth and A. J. Dennis, eds., Battelle Press, Columbus, OH., 1980, pp. 107-125.
72. Grimmer, G., K.-W. Naujack and D. Schneider. Profile Analysis of Polycyclic Aromatic Hydrocarbons by Glass Capillary Gas Chromatography in Atmospheric Suspended Particulate Matter in the Nanogram Range Collecting 10 m³ of Air. Fresenius Z. Anal. Chem., 311: 475-482, 1982.
73. Lee, M. L., G. P. Prado, J. B. Howard, and R. A. Hites. Source Identification of Urban Airborne Polycyclic Aromatic Hydrocarbons by Gas Chromatographic Mass Spectrometry and High Resolution Mass Spectrometry. Biomed. Mass Spectro., 4: 182-186, 1977.
74. Fox, M. A., and Staley, S. W. Determination of Polycyclic Aromatic Hydrocarbons in Atmospheric Particulate Matter by High Pressure Liquid Chromatography Coupled with Fluorescence Techniques. Anal. Chem., 48: 992-998, 1976.
75. Kebbekus, B., A. Greenberg, L. Morgan, J. Bozzelli, F. Darack, C. Eveleens, and L. Strangeland. Concentration of Selected Vapor and

- Particulate-phase Substances in the Lincoln and Holland Tunnels. J. Air Pollut. Control Assoc., 33: 328-330, 1983.
76. Daisey, J. M., J. Butler, and S. V. Hering. Unpublished Data, Manuscript in preparation.
 77. Handa, T., Y. Kato, T. Yamamura, T. Ishii, and H. Matsusheta. In Situ Emission Levels of Polynuclear Aromatic Hydrocarbons from Gasoline and Diesel Engine Vehicles on an Express Way. J. Environ. Sci. Health (A), 15: 573-599, 1980.
 78. Handa, T., Y. Kato, T. Yamamura, T. Ishii, and K. Suda. Correlation Between the Concentrations of Polynuclear Aromatic Hydrocarbons and Those of Particulates in Urban Atmosphere. Environ. Sci. Technol., 14: 416-422, 1980.
 79. Grimmer, G., H. Bohnke, and A. Glaser. Investigation on the Carcinogenic Burden by Air Pollution in Man. XV. Polycyclic Aromatic Hydrocarbons in Automobile Exhaust Gas - An Inventory. Zbl. Bakt. Hyg., I. Abt. Orig. B, 164: 218-234, 1977.
 80. Janssen, O. A Brief Review of Investigations on PAH in Vehicle Exhaust, Round Robin Tests on Profile Analysis, Role of Fuels and Lubricants, Field Studies. VDI-Berichte, nr., 358: 69-79, 1980.
 81. Spindt, R. S. First Annual Report on Polynuclear Aromatic Content of Heavy Duty Diesel Engine Exhaust Gases, Gulf Research and Development Co., prepared for Coordinating Research Council, Inc., EPA Contract No. 68-01-2116, 1974.
 82. Spindt, R. S. Second Year Report on Polynuclear Aromatic Content of Heavy Duty Diesel Engine Exhaust Gases, Prepared for the Coordinating Research Council, Inc. CRC APRAC Contract CAPE-24-72, Gulf Research and Development Co., Pittsburgh, PA. 15230, 1977.
 83. Springer, K. J., and T. M. Baines. Emissions from Diesel Versions of Production Passenger Cars. SAE Paper No. 770818, Society of Automotive Engineers, Warrendale, PA. 15096, 1977.
 84. Bricklmeyer, B. A., and R. S. Spindt. Measurement of Polynuclear Aromatic Hydrocarbons in Diesel Exhaust Gases, SAE Paper No. 780115, Society of Automotive Engineers, Inc., Warrendale, PA. 15096, 1978.
 85. Perez, J. M. Measurement of Unregulated Emissions: Some Heavy Duty Diesel Engine Results. Environ. Int., 5: 217-228, 1981.
 86. Hites, R. A., M.-L. Yu and W. G. Thilly. Compounds Associated with Diesel Exhaust Particulates. In: Chemical Analysis and Biological Fate:

- Polynuclear Aromatic Hydrocarbons, M. Cooke and A. J. Dennis, eds., 1981, pp. 455-466.
87. Choudhury, D. R., and B. Bush. Polynuclear Aromatic Hydrocarbons in Diesel Emission Particulates. Environ. Int., 5: 229-233, 1981.
 88. Schuetzle, D., F. S.-C. Lee, T. J. Prater, and S. B. Tejada. The Identification of Polynuclear Aromatic Hydrocarbon Derivatives in Mutagenic Fractions of Diesel Particulate Extracts. Intern. J. Environ. Anal. Chem., 9: 93-144, 1981.
 89. Hering, S. V., A. H. Miguel, and R. L. Dod. Tunnel Measurements of the PAH, Carbon Thermogram and Elemental Source Signature for Vehicular Exhaust. Paper presented at the Second International Conference on Carbonaceous Particles in the Atmosphere, Linz, Austria, Sept. 11-14, 1983.
 90. Szkarlat, A. C., and S. M. Japar. Optical and Chemical Properties of Particle Emissions from On-road Vehicles. J. Air Pollut. Control Assoc., 33: 592-597, 1983.
 91. Cha, S., D. Stiles, and R. Carlson. Investigation of Emissions from New-Design Oil-Fires Residential Heating Units. Report No. TR-81-22 prepared for Mobile Source Emissions Research Branch, U.S. Environmental Protection Agency, Research Triangle Park, N.C., Contract No. 68-02-2566, by Northrup Services, Inc., Research Triangle Park, N.C. 27709, 1981.
 92. Castaldini, C., R. A. Brown, and K. J. Lim. Combustion Modification Controls for Residential and Commercial Heating Systems, Vol. II: Oil-Fired Residential Furnace Field Test, EPA 600-7-81-123b, 1981.
 93. Sanborn, C. R., M. Cooke, W. E. Bresler, and M. C. Osborne. Characterization of Emissions of PAH's from Residential Coal-Fired Space Heaters. Paper No. 83-54.4, presented at the 76th Annual Meeting of the Air Pollution Control Association, Atlanta, GA., June 19-24, 1983.
 94. Truesdale, R. S., and J. G. Cleland. Residential Stove Emissions from Coal and Other Alternate Fuels. In: Proceedings Residential Wood and Coal Combustion, APCA Specialty Conference, March 1982, pp. 115-128.
 95. Cooke, W. M., J. M. Allen, and R. E. Hall. Characterization of Emissions from Residential Wood Combustion Sources. In: Residential Solid Fuels, J. A. Cooper and D. Malek, eds., Oregon Graduate Center, OR., 1982, pp. 139-163.
 96. Manning, J. A., R. E. Imhoff, M. V. Cooke, and T. L. Hayes. Ambient PAH and Residential Wood Combustion. Paper presented at the Poster Session

of the Sixth International Symposium on Polynuclear Aromatic Hydrocarbons, Battelle Columbus Laboratories, Oct. 27-29, 1981.

97. Inhoff, R. E., J. A. Manning, W. M. Cooke, T. L. Hayes. Final Report on a Study of the Ambient Impact of Residential Wood Combustion in Petersville, Alabama. In: Proceedings. Residential Wood and Coal Combustion, Specialty Conference, March, 1982, pp. 161-188.
98. DeAngelis, D. G., D. S. Ruffin, J. A. Peters, and R. B. Reznik. Source Assessment: Residential Combustion of Wood, EPA-600/1-80-042b, U.S. Environmental Protection Agency, Washington, D.C., 1980, 91 pp.
99. Allen, J. M., and W. M. Cooke. Control of Emissions from Residential Wood Burning by Combustion Modification, EPA-600/7-81-091, U.S. Environmental Protection Agency, Washington, D.C., 1981, 92 pp.
100. Peters, J. A., T. W. Hughes, and D. G. DeAngelis. Wood Combustion Emissions at Elevated Altitudes. In: Residential Solid Fuels, J. A. Cooper and D. C. Makel, eds., Oregon Graduate Center, OR., 1982, pp. 199-209.
101. Lea, R. C., R. S. Thomas, M. Lanoy, and S. WinLee. Investigation of PAH and Polychlorinated Organic Pollutant Emissions from Wood Combustion Sources. In: Polynuclear Aromatic Hydrocarbons: Formation, Metabolism and Measurement, M. Cooke and A. J. Dennis, eds., Battelle Press, Columbus, OH., 1983, pp. 745-755.
102. Knight, C. V., M. S. Graham, and B. S. Neal. Polynuclear Aromatic Hydrocarbons and Associated Organic Emissions for Catalytic and Noncatalytic Wood Heaters. In: Polynuclear Aromatic Hydrocarbons: Formation, Metabolism and Measurement, M. Cooke and A. J. Dennis, eds., Battelle Press, Columbus, OH., 1983, pp. 689-710.
103. Peters, J. A., D. G. DeAngelis, and T. W. Hughes. An environmental Assessment of POM Emissions from Residential Wood-Fired Stoves and Fireplaces. In: Polynuclear Aromatic Hydrocarbons: Chemical Analysis and Biological Fate, M. Cooke and A. J. Dennis, eds., Battelle Press, Columbus, OH., 1981, pp. 571-581.
104. Ramdahl, T., and G. Becher. Characterization of Polynuclear Aromatic Hydrocarbon Derivatives in Emissions from Wood and Cereal Straw Combustion. Anal. Chim. Acta, 144: 83-91, 1982.
105. Bennett, R. L., K. T. Knapp, P. W. Jones, J. E. Wilkerson, and P. E. Strup. Measurement of Polynuclear Aromatic Hydrocarbons and Other Hazardous Organic Compounds in Stack Gases. In: Polynuclear Aromatic Hydrocarbons, P. W. Jones and P. Leber, eds., Ann Arbor Science Publishers, Inc., Ann Arbor, MI. 48106, 1979, pp. 419-428.

106. Cuffe, S. T., R. W. Gerstle, A. A. Orning, and C. H. Schwartz. Air Pollutant Emissions from Coal-Fired Power Plants, Report No. 1. J. Air Pollut. Control Assoc., 14: 353-362, 1964.
107. Gerstle, R. W., S. T. Cuffe, A. A. Orning, and C. H. Schwartz. Air Pollutant Emissions from Coal-Fired Power Plants, Report No. 2. J. Air Pollut. Control Assoc., 15: 59-64, 1965.
108. Natusch, D. F. S. Potentially Carcinogenic Species Emitted to the Atmosphere by Fossil-fueled Power Plants. Environ. Health Pers., 22: 79-90, 1978.
109. Haile, C. L., J. S. Stanley, A. M. Magin, R. V. Northcull, and D. P. Redford. Emissions of Organic Pollutants from Coal-Fired Utility Boiler Plants. Chapter 27. In: Identification and Analysis of Organic Pollutants in Air, L. H. Keith, ed., Ann Arbor Science Publishers, Inc., Ann Arbor, MI., In Press.
110. Burlingame, J. O., J. E. Gabrielson, P. L. Langsjoen and W. M. Cooke. Field Tests of Industrial Coal Stoker Fired Boilers for Inorganic Trace Element and Polynuclear Aromatic Hydrocarbon Emissions, EPA-600/7-81-167, 1981.
111. Bergstrom, J. G. T., G. Eklund, and K. Trzcinski. Characterization and Comparison of Organic Emissions from Coal, Oil and Wood Fired Boilers. In: Polynuclear Aromatic Hydrocarbons, Physical and Biological Chemistry, M. Cooke, A. J. Dennis, and G. L. Fisher, eds., Battelle Press, Columbus, OH., 1982, pp. 109-120.
112. Bjorseth, A., O. Bjorseth, and P. E. Fjeldstad. Polycyclic Aromatic Hydrocarbons in the Work Atmosphere. II. Determination in a Coke Plant. Scand. J. Work Environ. Health, 4: 224-236, 1978.
113. Bjorseth, A. Determination of Polynuclear Aromatic Hydrocarbons in the Working Environment. In: Polynuclear Aromatic Hydrocarbons, P. W. Jones and P. Leber, eds., Ann Arbor Science Publishers, Inc., Ann Arbor, MI., 1979, pp. 371-381.
114. Bjorseth, A., O. Bjorseth, and P. E. Fjeldstad. Polycyclic Aromatic Hydrocarbons in the Work Atmosphere. I. Determination in an Aluminum Reduction Plant. Scand. J. Work Environ. Health, 4: 212-223, 1978.
115. Evans, J. S., and D. W. Cooper. An Inventory of Particulate Emissions from Open Sources. J. Air Pollut. Control Assoc., 30: 1298-1303, 1980.
116. Cass, G. R., and G. J. McRae. Source-Receptor Reconciliation of Routine Air Monitoring Data for Trace Metals: An Emission Inventory Assisted Approach. Environ. Sci. Technol., 17: 129-139, 1983.

117. Shabad, L. M. Circulation of Carcinogenic Substances in the Environment: From Laboratory Experiments to Field Investigations. GANN Monograph on Cancer Research, 17: 179-187, 1975.
118. Grimmer, G. Environmental Carcinogens: Polycyclic Aromatic Hydrocarbons, CRC Press, Inc., Boca Raton, 1983.
119. Sims, R. C., and M. R. Overcash. Fate of Polynuclear Aromatic Compounds in Soil-Plant Systems. Residue Reviews, 88: 1-68, 1983.
120. Wang, D. T., and O. Meresz. Occurrence of Potential Uptake of Polynuclear Aromatic Hydrocarbons of Highway Traffic Origin by Proximally Grown Food Crops. In: Polynuclear Aromatic Hydrocarbons Physical and Biological Chemistry, M. Cooke, A. J. Dennis, and G. L. Fisher, eds., Battelle Press, Columbus, OH., 1982, pp. 885-896.
121. Butler, J. D., V. Butterworth, S. C. Keldow, and H. G. Robinson. Some Observations on the Polycyclic Aromatic Hydrocarbon (PAH) Content of Surface Soils in Urban Areas. Sci. Total Environ., 33: 75-85, 1984.
122. Hauser, T. R., and J. N. Pattison. Analysis of Aliphatic Fraction of Air Particulate Matter. Environ. Sci. Technol., 6: 549-555, 1972.
123. Teraniski, K., K. Hamada, and H. Watanabe. Mutagenicity in Salmonella typhimurium Mutants of the Benzene-Soluble Organic Matter Derived from Airborne Particulate Matter and its Fine Fractions. Mutat. Res., 56: 273-280, 1978.
124. Ketserides, G., J. Hahn, R. Jaenicke, and C. Junge. The Organic Constituents of Atmospheric Particulate Matter. Atmos. Environ., 10: 603-610, 1976.
125. Simoneit, B. R. T., and M. A. Mazurek. Organic Matter of the Troposphere II. Natural Background of Biogenic Lipid Matter in Aerosols Over the Rural Western United States. Atmos. Environ., 16: 2139-2159, 1982.
126. Wils, E. R. J., A. G. Hulst, and J. C. den Hartog. The Occurrence of Plant Wax Constituents in Airborne Particulate Matter in an Urbanized Area. Chemosphere, 11: 1087-1096, 1982.
127. Broddin, G., W. Cautreels, and K. Van Cauwenberghe. On the Aliphatic and Polyaromatic Hydrocarbon Levels in Urban and Background Aerosols from Belgium and the Netherlands. Atmos. Environ., 14: 895-910, 1980.
128. Griest, W. H., and M. R. Guerin. Identification and Quantification of Polynuclear Organic Matter on Particulates from a Coal-Fired Power Plant, Interim Report EA-1092 on Research Project 1057-1 (DOE No. RTS

- 77-58), prepared for the Electric Power Research Institute, Palo Alto, CA., 94304, 1979.
129. Simoneit, B. R. T., M. A. Mazurek, and W. E. Reed. Characterization of Organic Matter in Aerosols Over Rural Sites: Phytosterols. Paper presented at the Tenth International Meeting on Organic Geochemistry, Bergen, Norway, Sept. 14-18, 1981.
 130. Sawicki, E., J. E. Meeker, and M. J. Morgan. The Quantitative Composition of Air Pollution Source Effluents in Terms of Aza Heterocyclic Compounds and Polynuclear Aromatic Hydrocarbons. Int. J. Air Wat. Poll., **9**: 291-298, 1965.
 131. Dong, M. W., D. C. Locke, and D. Hoffmann. Characterization of Aza-Arenes in Basic Organic Portion of Suspended Particulate Matter. Environ. Sci. Technol., **11**: 612-618, 1977.
 132. Mobile Source Research Committee. The Diesel Emissions Research Program, Report No. EPA-625/9-79-004, 1979.
 133. Gibson, T. L. Preliminary Communication: Nitro Derivatives of Polynuclear Aromatic Hydrocarbons in Airborne and Source Particulate Matter. Atmos. Environ., **16**: 2037-2040, 1982.
 134. Gibson, T. L. Sources of Direct-Acting Nitroarene Mutagens in Airborne Particulate Matter. Mutat. Res., **122**: 115-121, 1983.
 135. Jin, Z., and S. M. Rappaport. Microbore Liquid Chromatography with Electrochemical Detection for Determination of Nitro-Substituted Polynuclear Aromatic Hydrocarbons in Diesel Soot. Anal. Chem., **55**: 1778-1781, 1983.
 136. Cautreels, W., and K. Van Cauwenberghe. Determination of Organic Compounds from Airborne Particulate Matter by Gas Chromatography Mass Spectrometry. Atmos. Environ., **10**: 447-457, 1976.
 137. Cautreels, W., K. Van Cauwenberghe, and L. A. Guzman. Comparison Between the Organic Fraction of Suspended Matter at a Background and an Urban Station. Sci. Total Environ., **8**: 79-88, 1977.
 138. Van Vaeck, L., G. Broddin, and K. Van Cauwenberghe. Differences in the Particle Size Distributions of Major Organic Pollutants in Ambient Aerosols in Urban, Rural and Seaside Areas. Environ. Sci. Technol., **13**: 1494-1509, 1979.
 139. Schuetzle, D., D. Cronn, A. L. Crittenden, and R. L. Charlson. Molecular Composition of Secondary Aerosol and Its Possible Origin. Environ. Sci. Technol., **9**: 838-845, 1975.

140. Cronn, D. R., R. J. Charlson, R. L. Knights, A. L. Crittenden, and B. R. Appel. A Survey of the Molecular Nature of Primary and Secondary Components of Particles in Urban Air by High Resolution Mass Spectrometry. Atmos. Environ., 11: 929-937, 1977.
141. Grosjean, D., K. Van Cauwenberghe, J. P. Schmid, P. E. Kelley, and J. N. Pitts, Jr. Identification of C₃-C₁₀ Aliphatic Dicarboxylic Acids in Airborne Particulate Matter. Environ. Sci. Technol., 12: 313-316, 1978.
142. Yasuhara, A., and K. Fuwa. Determination of Fatty Acids in Airborne Particulate Matter, Dust and Soot by Mass Chromatography. J. Chromatogr., 240: 369-376, 1982.
143. Vick, R. D., G. A. Junk, M. J. Avery, J. J. Richard, and H. J. Svec. Organic Emissions from Combustion of Combination Coal/Refuse to Produce Electricity. Chemosphere, 11: 893-902, 1978.
144. Haile, C. L., J. S. Stanley, R. M. Lucas, D. K. Melroy and W. L. Yauger, Jr. Pilot Study of Information of Specific Compounds from Combustion Sources, report prepared for the Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency, Contract No. 68-01-5915, 1983.
145. Currie, L. A. Contemporary Particulate Carbon. In: Particulate Carbon: Atmospheric Life Cycle, G. T. Wolff and R. L. Klimisch, eds., Plenum Press, New York, 1982, pp. 245-260.
146. Cooper, J. A., L. A. Currie, and G. A. Klouda. Assessment of Contemporary Carbon Combustion Source Contributions to Urban Air Particulate Levels Using Carbon-14 Measurements. Environ. Sci. Technol., 15: 1045-1050, 1981.
147. Dasch, J. M. Particulate and Gaseous Emissions from Woodburning Fireplaces. Environ. Sci. Technol., 16: 639-645, 1982.
148. Soderberg, R. H., J. F. Hornig, A. Barefoot, and C. Parravano. Measurements of Polycyclic Aromatic Hydrocarbons in Ambient Air Particulates in Northern New England. Paper presented at the Air Pollution Control Association Conference, Chicago, Ill., March 22-25, 1983.
149. Hornig, J. F., R. H. Soderberg, A. C. Barefoot, and J. F. Galasyn. Woodsmoke Analysis: Vaporization Losses of PAH from Filters and Levoglucosan As a Distinctive Marker for Woodsmoke. Paper presented at the eighth International Symposium on Polynuclear Aromatic Hydrocarbons, Battelle Columbus Laboratory, Columbus, OH., 1983.

150. Pictet, A., J. Sarasin. Sur la distillation de la cellulose et de l'amidon sous pression reduite. Helv. Chim. Acta, 1: 87, 1918.
151. Ramdahl, T. Retene - A Molecular Marker of Wood Combustion in Ambient Air. Nature, 306: 580-582, 1983.
152. Thrane, K. E., and L. Wikstrom. Monitoring of Polycyclic Aromatic Hydrocarbons in Ambient Air. Paper presented at the 8th International Symposium on Polynuclear Aromatic Hydrocarbons, Battelle, Columbus Laboratories, Columbus, OH., 1983.
153. Hopke, P. K. Application of Factor Analysis to Quantitative Source Apportionment. In: Atmospheric Aerosols: Source/Air Quality Relationships ACS Symposium Series No. 167, E. S. Mascias and P. K. Hopke, eds., American Chemical Society, Washington, D.C., 1981, pp. 21-49.
154. Hopke, P. K., D. J. Alpert, and B. A. Roscoe. FANTASIA - A Program for Target Transformation Factor Analysis to Apportion Sources in Environmental Samples. Computers and Chemistry, 7: 149-155, 1983.
155. a. Nie, N. H., C. H. Hall, J. G. Jenkins, K. Steinbrenner, and D. H. Bent. SPSS Statistical Package for the Social Sciences, 2nd ed., McGraw-Hill Book Co., New York, N.Y., 1975.
- b. Hull, C. H., and N. H. Nie, eds., SPSS Update. New Procedures and Facilities for Releases 7 and 8. McGraw-Hill Book Co., New York, N.Y., 1979.
156. Roscoe, B. A., P. K. Hopke, S. L. Dattner, and J. M. Jenks. The Use of Principal Component Factor Analysis to Interpret Particulate Compositional Data Sets. J. Air Pollut. Control Assoc. 32: 637-642, 1982.
157. Daisey, J. H., M. Morandi, G. T. Wolff, and P. J. Liou. Regional and Local Influences on the Nature of Airborne Particulate Organic Matter at Four Sites in New Jersey During Summer, 1981. Atmos. Environ., 18: 1411-1419, 1984.
158. Samples of particulate matter collected in the Allegheny Tunnel during the summer of 1979 were provided by Dr. William Pierson of Ford Motor Company. Portions of each sample were extracted sequentially with cyclohexane and dichloromethane to determine extractable organic masses. A second aliquot of each was analyzed for lead.
159. Manhattan River Crossings, Traffic Volume, 1979. Report prepared by the New York City Dept. of Transportation, February, 1981.

160. New York City Bridge Traffic Volumes, 1980. Report prepared by the New York City Dept. of Transportation, 1982.
161. Gartrell, G., and S. K. Friedlander. Relating Particulate Pollution to Source: The 1972 Aerosol Characterization Study. Atmos. Environ., 9: 279-299, 1972?
162. Watson, J. G., Jr. Chemical Element Balance Receptor Model Methodology for Assessing the Sources of Fine and Total Suspended Particulate Matter in Portland, Oregon. Ph.D. Thesis, Oregon Graduate Center, Beaverton, OR., 1979.
163. Grosjean, D. Solvent Extraction and Organic Carbon Determination in Atmospheric Particulate Matter: The Organic Extraction-Organic Carbon Analyzer (OE-OCA, technique. Anal. Chem., 47: 797-805, 1975.
164. Liroy, P. J., T. J. Kneip, and J. M. Daisey. The Measurement of Particulate Organic Matter at a Non-Urban Site in the Northeast. J. Geophys. Res., In Press.
165. Schwartz, G. P., J. M. Daisey, and P. J. Liroy. Effect of Sampling Duration on the Concentration of Particulate Organics Collected on Glass Fiber Filters. Amer. Ind. Hyg. Assoc. J., 42: 258-263, 1981.
166. Draper, N. R., and H. Smith. Applied Regression Analysis, 2nd ed., John Wiley and Sons, New York, 1981.
167. Junge, C. E. Basic Considerations About Trace Constituents in the Atmosphere as Related to the Fate of Global Pollutants. In: Fate of Pollutants in the Air and Water Environment, I. H. Suffet, ed., Wiley-Interscience, New York, 1977, pp. 7-25.
168. Cupitt, L. T. Fate of Toxic and Hazardous Materials in the Air Environment, Report No. EPA-600/3-80-084, PB 80-221948, 1980.
169. Corn, M., T. L. Montgomery and N. A. Esmen. Suspended Particulate Matter: Seasonal Variation in Specific Surface Areas and Densities. Environ. Sci. Technol., 5: 155-158, 1971.
170. Handbook of Chemistry and Physics, 42nd ed., C. D. Hodgman, R. C. Weast, and S. M. Selby, eds., The Chemical Rubber Publishing Co., Cleveland, OH., 1960.

171. Daisey, J. M., C. F. Allen, G. McGarrity, T. Atherholt, J. Louis, L. McGeorge, and P. J. Liou. Effects of Filter Type on the Organic Composition and Mutagenicity of Inhalable Particulate Matter. Extended Abstract. Aerosol Sci. Technol., 2: 295, 1983. Full manuscript in preparation.
172. Simoneit, B. R. T., and M. A. Mazurek. Organic Matter of the Troposphere: II. Natural Background of Biogenic Lipid Matter in Aerosols over the Rural Western United States. Atmos. Environ., 16: 2139-2159, .
173. Daisey, J. M., M. A. Leyko, M. T. Kleinman, and E. Hoffman. The Nature of the Organic Fraction of the New York City Summer Aerosol. Ann. N.Y. Acad. Sci., 322: 125-142, 1979.
174. Gabriels, R. A General Method for Calculating the Detection Limit in Chemical Analysis. Anal. Chem., 42: 1439-1440, 1970.

APPENDIX A

Schematic Diagrams of Source Sampling Trains
Commonly used for Sampling Stationery Sources

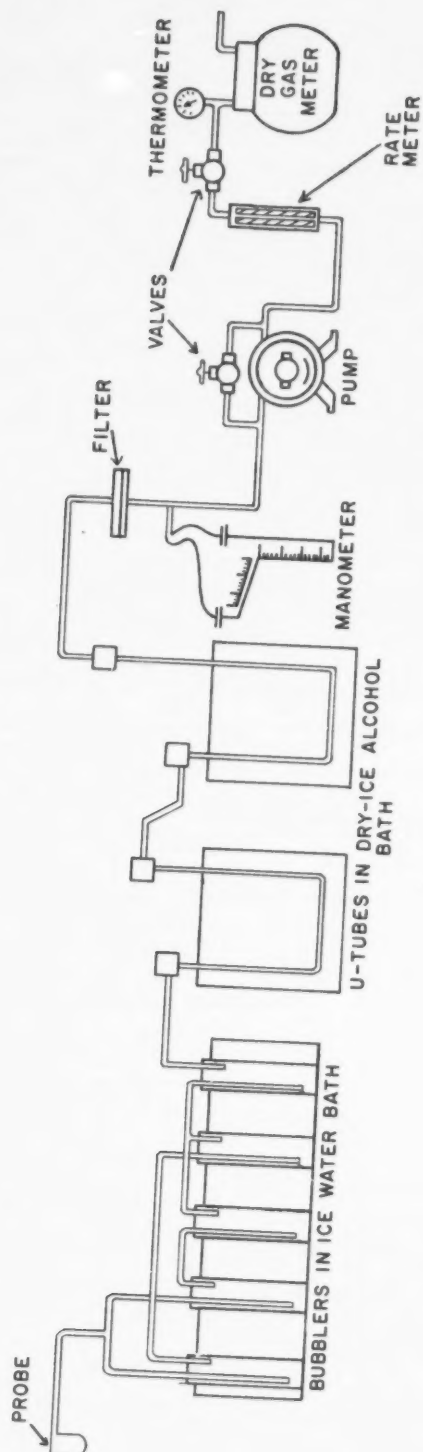


Figure A-1. Polynuclear Hydrocarbon Sampling Train used by Cuffe et al., J. Air Pollut. Contr. Assoc., 14: 9 (1964).

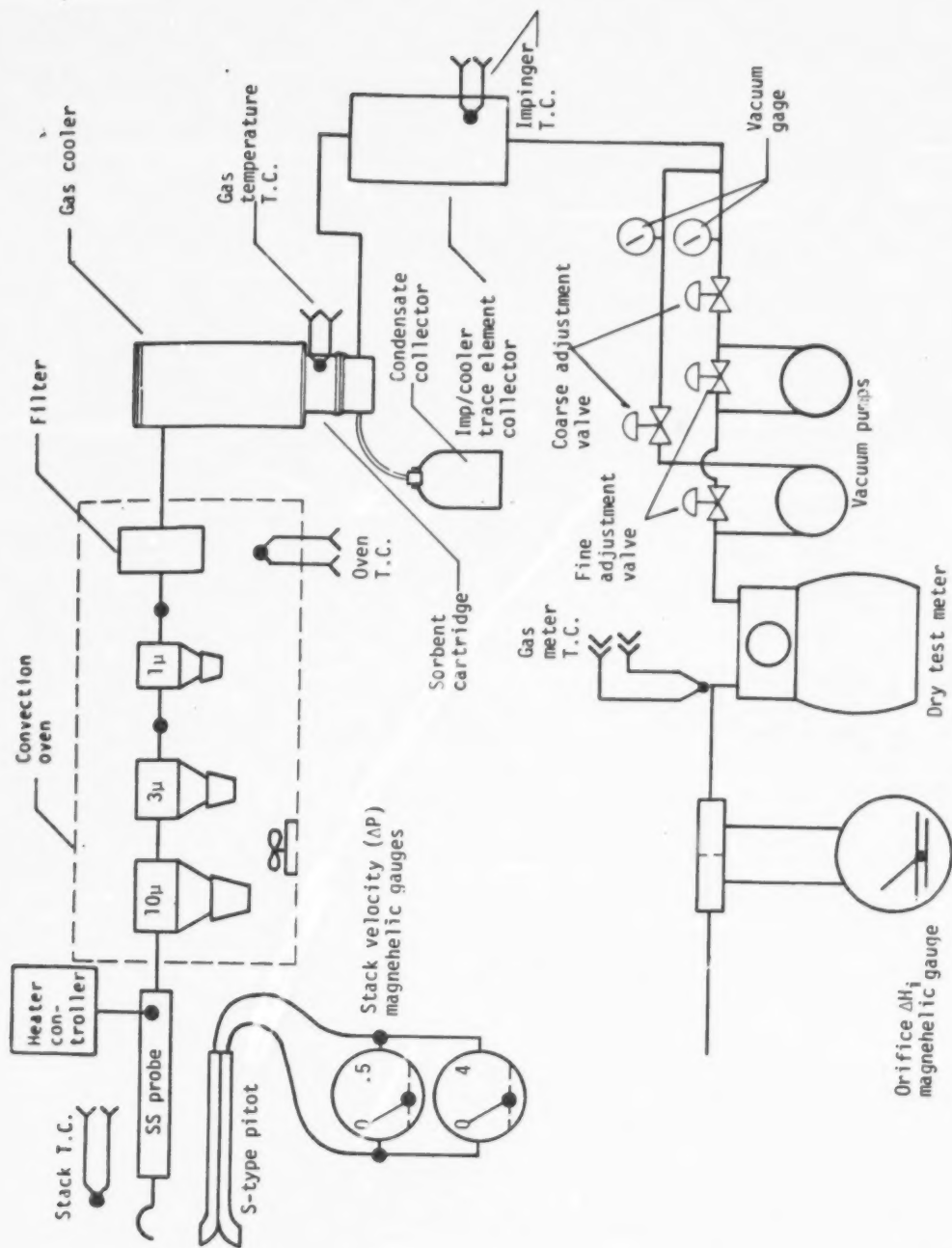
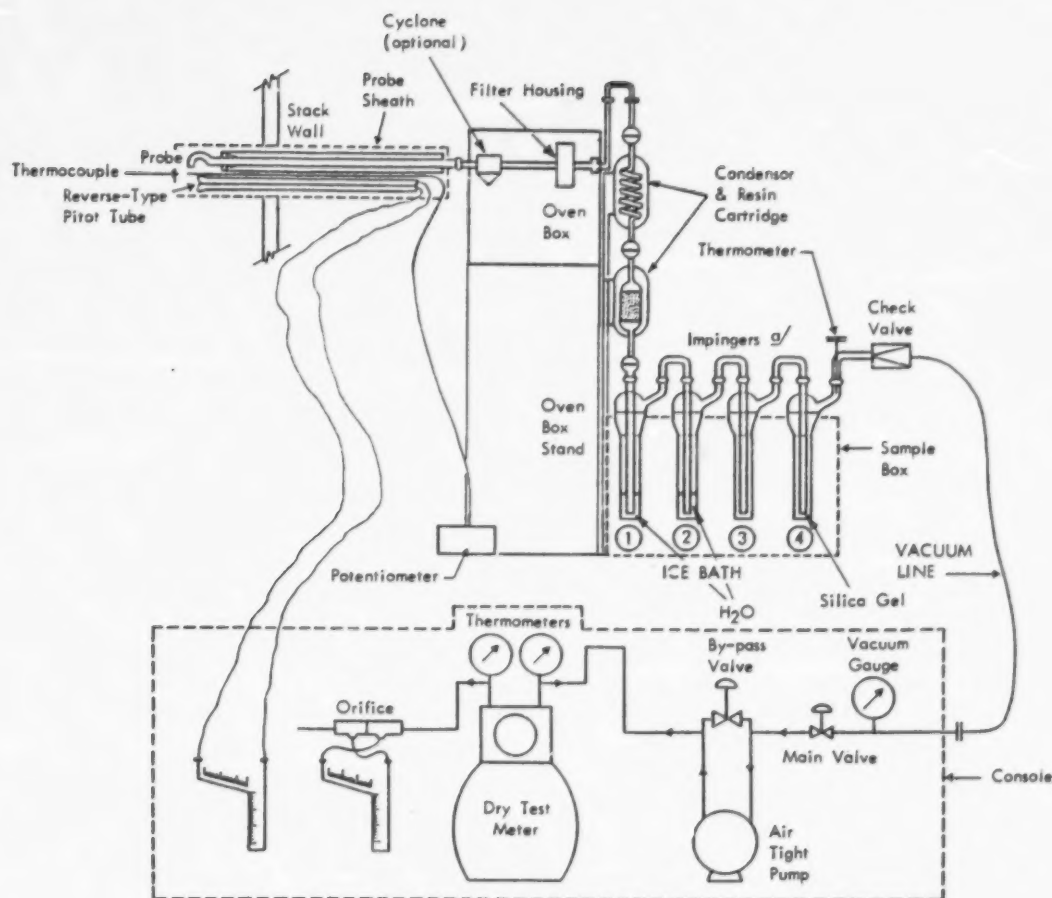


Figure A-2. SASS Train.



- a/ Impingers 1, 3 and 4 are of the Modified Greenburg-Smith Type
 Impinger 2 is of the Greenburg-Smith Design
 Impinger 1 and 2 Contain 100 ml Water
 Impinger 3 Empty
 Impinger 4 Contains 200-300 Grams Silica Gel

Figure A-3. Modified Method 5 train for organics sampling.

APPENDIX B

METHODS OF SAMPLE COLLECTION

B.1 New York City

The sampling site in New York City was located at New York University Medical Center, in Manhattan, on East 30th Street between First Avenue and the FDR Drive. The station was located on top of the residence hall, about 70 m above ground level.

The fully automated constant flow samplers used for the collection of weekly samples of respirable (1) suspended particulate matter (RSP) [$\leq 3.5 \mu\text{m}$ aerodynamic diameter] is diagrammed in Figure B-1. It employs a Roots-Connersville Model 33AF blower. A bypass valve at the inlet to the pump is accurately regulated to maintain a constant flow of air through an Aerotec-2 cyclone and the filter. The flow rate across the filter is metered by measuring the differential pressure across a sharp edge orifice placed between the filter and the pump. A photohelic gauge and switch is used to control an electric actuator which rotates the bypass valve. When the flow rate decreases below a preset value, the valve is actuated to close. As it closes, the flow rate across the filter is increased. When the pressure drop across the orifice has increased sufficiently, the control then de-energizes the valve actuator. Should the flow increase during sampling, such as might occur following a large decrease in humidity, the control will energize the valve actuator to open the bypass, thereby decreasing the flow across the filter. The air entering the bypass system is filtered using a disposable carburetor filter to protect the pump and ball valve assembly from airborne dirt.

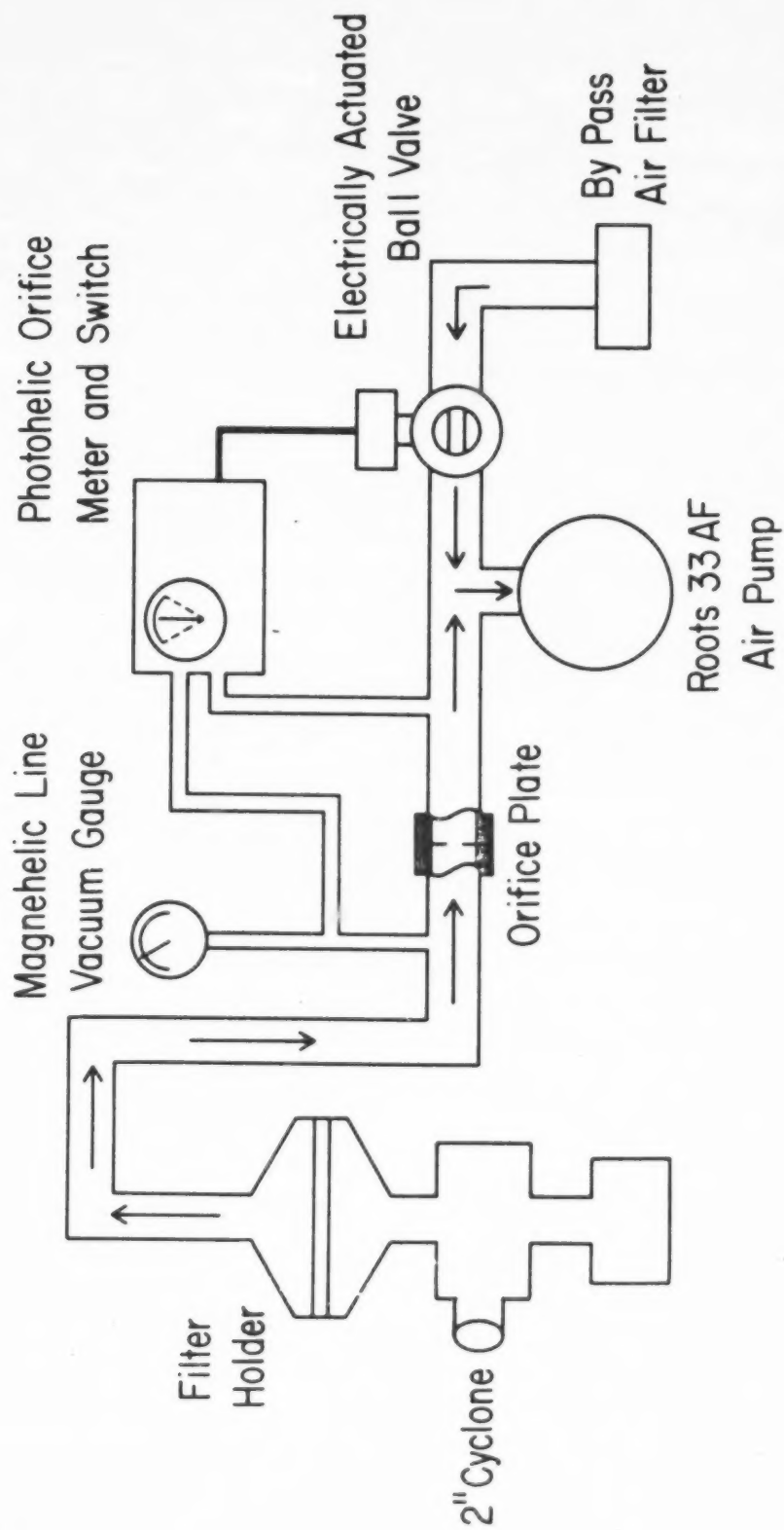


Figure B-1. Block Diagram of Sampling System.

Bypass control was accomplished with a 3.8 cm I.D. Hills-McCanna valve and a Ramoon 8BR actuator. The orifice meter was constructed from 5.08 cm galvanized pipe, with a one-inch orifice plate set onto a pipe union machined to it. Pressure taps of 1 cm pipe were set 5 cm upstream, and 2.5 cm downstream, of the orifice plate. A 90 cm long straight pipe is inserted between the sampler head and the orifice to eliminate effects of upstream bends or constrictions on the flow profile within the pipe. The sensor for the control is a 0-5 inch (water) Dwyer Photohelic; essentially a Magnehelic differential pressure gauge to which photocells and a light have been attached. The photocells activate switches which control the bypass valve. Control settings are adjusted with pointers on the face of the gauge.

Aerotec-2 cyclones were used as precollectors for particles larger than 3.5 μm aerodynamic diameter. Flow through the cyclone was maintained at 0.45 m^3/min in order to get a 3.5 μm "cut" (2). The cyclones were calibrated in the Laboratory of Aerosol Research at the Institute of Environmental Medicine, N.Y.U. Medical Center (3).

Each orifice meter was calibrated with a Venturi meter which has been previously calibrated with a spirometer. Orifice meter calibrations were made by attaching the Venturi meter followed by a valve in place of the filter, upstream of the system orifice meter and pump assembly. the pump was started and the line static pressure and pressure drop across the orifice were recorded together with the flow rate. A least-squares multiple regression equation was fitted for flow rate as a function of the square roots of static pressure and pressure drop across the orifice.

The calibrations for all sampling systems are routinely checked on an annual basis, although no significant changes in the calibration curves have been observed over the past 12 years.

Two weekly (7 day) samples of RSP were collected from August, 1978 to November, 1981. One sample, collected on Gelman Spectrograde filters, was used to determine particle mass, trace elements and water-soluble sulfate. The second sample was collected on Gelman Type AE glass fiber filters, pre-ignited at 400°C for 48 hrs. in a muffle oven, to remove organic contaminants. These filters were wrapped in aluminum foil for storage. Filters were unwrapped and loaded into a cartridge filter holder on a sheet of "tea" paper for filter changes in the field. Both the cyclones and filters were replaced on a weekly basis.

Loaded filters were removed from the cartridge and wrapped in aluminum foil so that the particulate matter was shielded from light. The filters were stored overnight in a styrofoam cooler placed in a cold room (0°C) at the Medical Center and then the cooler (and sample) were transported via courier to the A. J. Lanza Laboratory in Tuxedo. Each sample was accompanied by a sample collection data sheet. A frozen ice pack inside the cooler maintained a low temperature during transport. The samples were stored in a freezer at -20°C prior to extraction. Average storage time was one to two weeks.

B.2 Philadelphia Samples

As part of the Philadelphia Model Evaluations Study of 1982, 24 hour samples of inhalable ($\leq 15 \mu\text{m}$, A.D.) particulate matter (IPM) were collected for organic analyses at the Fireboat Station in Philadelphia, PA. The sampler

was provided by the Philadelphia Division of Air Management and calibrated by New York University Medical Center personnel. Pedco personnel collected the samples daily and transferred them to the ATEOS (3) sampling site at the Institute of Medical Research in Camden. The transfers were made at intervals for shipment to the N.Y.U. Laboratories in Tuxedo, N.Y. along with the ATEOS (3) samples. The samples were stored in a freezer and shipped with cold packs (0°C). Upon receipt at N.Y.U., the samples were stored overnight in a freezer at -30°C. Organic extractions were initiated within 24 hours of receipt of the samples. A summary of the samples collected is presented in Table B-1.

B.3 References

1. Lippmann, M. "'Respirable' Dust Sampling." Amer. Ind. Hyg. Assoc. J. 31: 138-158 (1970).
2. Lippmann, M. and T. L. Chan. "Calibration of Dual-Inlet Cyclones for "Respirable" Mass Sampling." Amer. Ind. Hyg. Assoc. J. 35: 189-200 (1974).
3. Liou, P. J., J. M. Daisey, T. Altherholt, J. Bozzelli, F. Darack, R. Fisher, A. Greenberg, R. Harkov, B. Kebbekus, T. J. Kneip, J. Louis, G. McGarrity, L. McGeorge and N. M. Reiss. "The New Jersey Project on Airborne Toxic Elements and Organic Substances (ATEOS): A Summary of the 1981 Summer and 1982 Winter Studies." APCA Journal 33(7): 649-657 (1983).

Table B-1. Philadelphia Sample Log (Samples for Organic Analyses)

<u>Filter No.</u>	<u>Date</u>	<u>Comments</u>
651	7/15-7/16/82	No tea paper to protect sample, sample damaged
652	7/16-7/17/82	Sample damaged-no tea paper
653	7/17-7/18/82	Incorrect flow setting, no tea paper, evidence of leak
654	7/18-7/19/82	Power failure; incorrect flow setting, poor sample handling
656	7/20-7/21/82	Incorrect flow, evidence of leak
658	7/21-7/22/82	Probable leak; filter misplaced on sampler
660	7/22-7/23/82	Probable leak; filter misplaced on sampler
661	7/23-7/24/82	Probable leak; filter misplaced on sampler, incorrect flow setting
662	7/24-7/25/82	Probable leak

Filters Nos. 651 to 658 were delivered 7/22/82.

663	7/25-7/26/82	Sample collected on wrong side of filter
664	7/26-7/27/82	Sample collected on wrong side of filter
665	7/27-7/28/82	Power failure
666	7/28-7/29/82	Sample collected on wrong side of filter
669	7/29-7/30/82	Sample collected on wrong side of filter
668	7/30-7/31/82	Sample collected on wrong side of filter
670	7/31-8/ 1/82	
671	8/ 1-8/ 2/82	Sample collected on wrong side of filter
672	8/ 2-8/ 3/82	Sample collected on wrong side of filter

Filters Nos. 660 to 671 were delivered on 8/2/82.

673	8/ 3-8/ 4/82	
674	8/ 4-8/ 5/82	
675	8/ 5-8/ 6/82	

Table B-1 Continued. Philadelphia Sample Log (Samples for Organic Analyses)

<u>Filter No.</u>	<u>Date</u>	<u>Comments</u>
676	8/ 6-8/ 7/82	
677	8/ 7-8/ 8/82	
678	8/ 8-8/ 9/82	
679	8/ 9-8/10/82	
680	8/10-8/11/82	Water blotch on portion of filter
682	8/11-8/12/82	Several water spots on filter
683	8/12-8/13/82	Filter completely wet
684	8/13-8/14/82	

The last set of filters were delivered by Federal Express on 8/17/82 and had not been kept cold.

APPENDIX C

ANALYSES FOR TRACE ELEMENTS AND WATER-SOLUBLE SULFATE

C.1 Analyses of Trace Metals at N.Y.U. by Atomic Absorption Spectrophotometry

An aliquot (2.54 cm x 20.3 cm) was cut from each New York City sample collected on the Spectrograde filters. The aliquots were placed into beakers and digested with a mixture of 50 ml of 5% $\text{HCIO}_4/\text{HNO}_3$ acid. The filters were stirred and stood overnight in the Perchloric acid hoods. The samples were heated and kept just below boiling point for about 2 hours. The solution was decanted into clean acid washed 250 ml beakers. This procedure was repeated, giving a total volume of about 125 ml in the second beaker. The sample was extracted a third time with 75 ml of deionized water. The combined extracts were evaporated gently and heated until the appearance of HCIO_4 fumes (3-5 minutes). The samples were then cooled, the solutions filtered, the residue, if any, was washed with deionized water, and the solution was diluted to exactly 25 ml with 5% HNO_3 .

To minimize blanks, redistilled acids and deionized water were used in all analyses. A series of blank and N.B.S. spiked filter samples were run through the same procedure with each set of filter samples. Trace metals were analyzed for Pb, Mn, Cu and V by atomic absorption spectrophotometry using an Instrumentation Laboratories 257 Atomic Absorption Spectrophotometer.

C.2 Analyses for Water-Soluble Sulfate

An aliquot (2.54 cm x 20.3 cm) of each sample collected on Spectrograde filters in New York City was analyzed for water-soluble sulfate using the

gravimetric method previously developed in this laboratory (1). Each sample was extracted four times with 200 ml of 90°C water for 30 minutes each time. The extracts were combined and passed through an ion exchange column containing Rexyn 101 (H⁺) to remove cations which could coprecipitate with BaSO₄. A portion of the eluant was then reacted with 1N BaNO₃ at 90°C for 30 minutes and then cooled. The BaSO₄ was filtered, dried in a dessicator to constant weight and then the weight was recorded.

C.3 XRF Analyses

Portions of the New York City RSP samples collected between 12/28/78 and 12/30/80 were analyzed for additional elements (S, Fe, Pb, Mo, P, Br, V, Ti, Ni) for the purpose of model development. The samples were analyzed by x-ray fluorescence analysis (2) at the Environmental Sciences Research Laboratory of the U.S. Environmental Protection Agency. Although this method is generally applied to low volume samples collected on cellulose membrane or Teflon filters (2), it was felt that with appropriate corrections, in situ analyses of high volume samples collected on Spectrograde filters would be possible. Since these same samples had been analyzed for Pb, V and water-soluble sulfate by N.Y.U. by a different method, an interlaboratory comparison was possible for these elements. Figures C-1 to C-3 show the correlation between the methods. The correlation coefficients were 0.84 and 0.93 for Pb and V, respectively. For Pb, 86% of all of the paired values fall within $\pm 20\%$ of the equivalence line. Sixty-nine out of 100 of the N.Y.U. Pb values were higher than those reported by EPA. The sign test (3) indicates that this is significant difference at the 1% level and that there may be a bias. Least

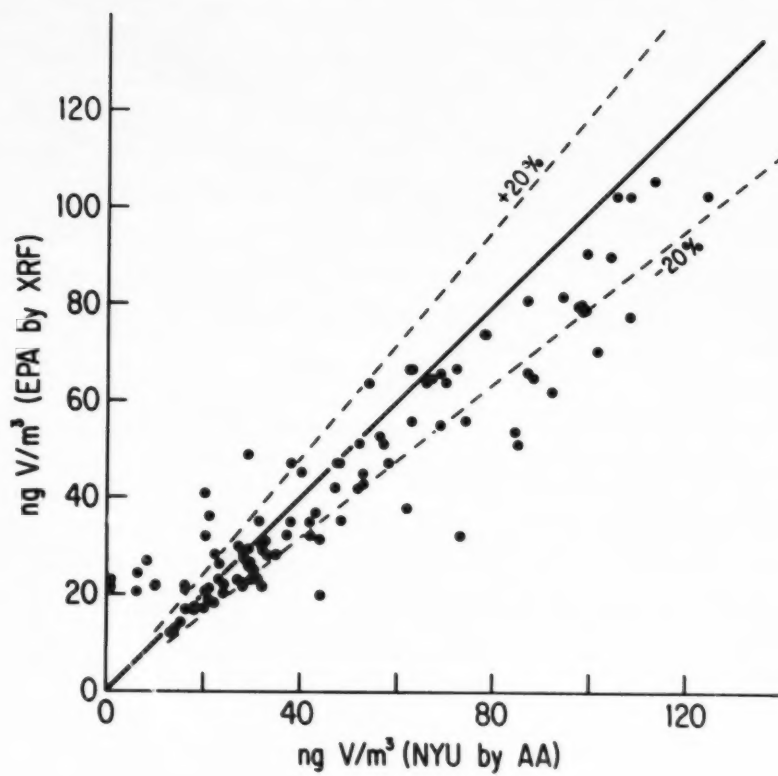


Figure C-1. RSP V - NYU Medical Center Station.

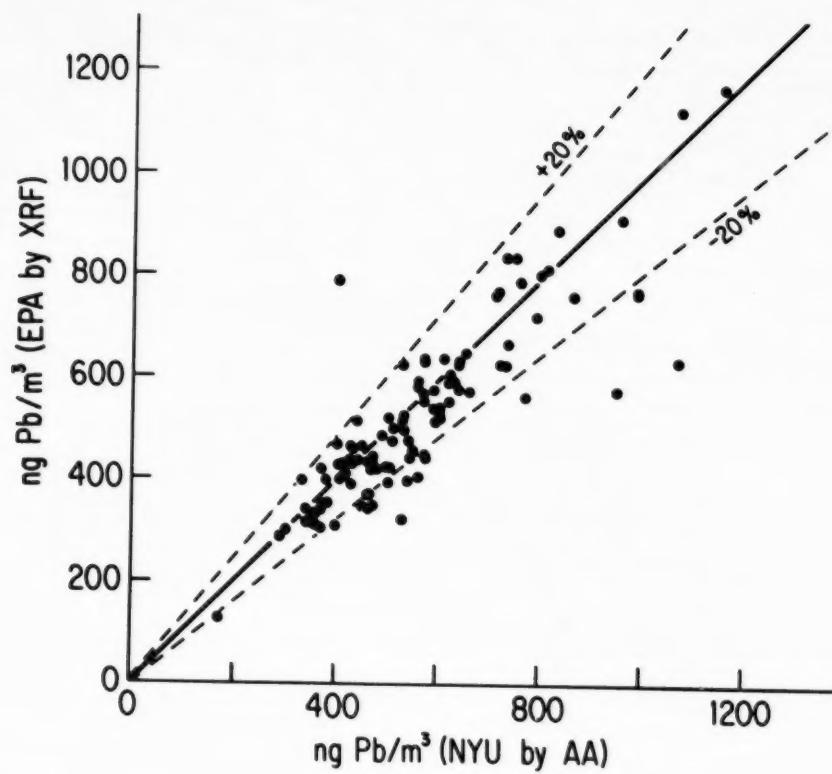


Figure C-2. RSP Pb - NYU Medical Center Station.

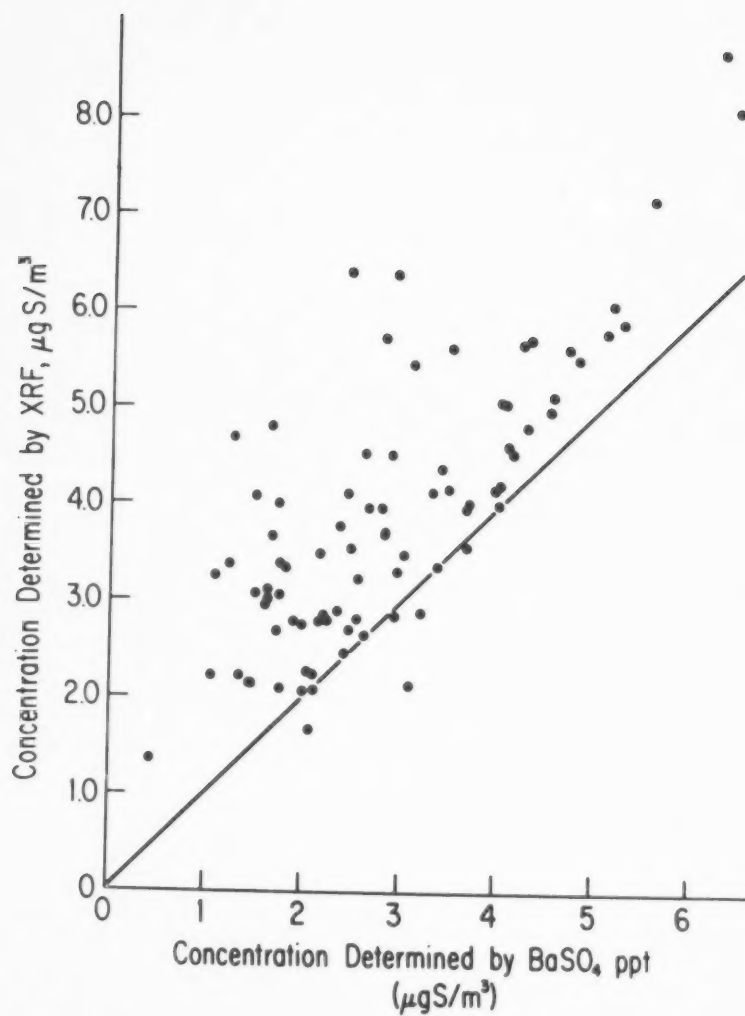


Figure C-3. RSP Sulfur - NYU Medical Center Station

squares analyses of the Pb data gives the following relationship between the two methods:

$$\text{Pb(EPA)} = 0.83 \text{ Pb(NYC)} + 63.0 \quad (1)$$

For V, the relationship between the two methods was:

$$\text{V(EPA)} = 0.72 \text{ V(NYU)} + 8.4 \quad (2)$$

Sixty-eight percent of the paired vanadium values fell within $\pm 20\%$ of the equivalence line. At the lower concentration, near the limits of detection, N.Y.U. generally reported lower values for V than did EPA; at higher concentrations, this pattern was reversed.

For the sulfur values, the concentrations determined by XRF are higher than those determined gravimetrically by precepitation of BaSO_4 . Analysis of the NBS Urban Particulate Standard Reference Material No. 1648 by the gravimetric method indicated only an $80 \pm 2\%$ recovery of sulfate by this method. If the N.Y.U. data are corrected for recovery, the relationship between the two methods is:

$$\text{S(XRF)} = 1.19 \text{ S(N.Y.U.)} - 0.34 \quad (3)$$

with a correlation coefficient of 0.76 ($n = 88$).

C.4 References

1. Eisenbud, M. and T. J. Kneip, Trace Metals in Urban Aerosols. Report No. RP-117 to the Electric Power Research Institute, Palo Alto, CA. NTIS Pub. No. 248-324, 1976.
2. Dzubay, T. G. and R. K. Stevens (1975) "Ambient air analysis with dichotomous sampler and x-ray fluorescence spectrometer," Environ. Sci. Technol., 9: 663-668.
3. Dixon, W. J. and F. J. Massey, Jr. Introduction to Statistical Analysis, 3rd ed., McGraw-Hill Book Co., New York, 1969.

APPENDIX D
METHODS OF ORGANIC ANALYSES

D.1 Extractions

Samples (i.e., New York City, Philadelphia, Caldecott Tunnel and NBS SRM 1649) were extracted sequentially with increasingly polar solvents, cyclohexane, dichloromethane and acetone. This scheme separates the organic compounds in suspended particulate matter into non-polar, moderately polar and polar fractions, respectively. Half of each loaded filter was extracted in a Soxhlet apparatus for 7.5 hours with 200 ml of each solvent. In the case of the NBS standard, 200 mg was wrapped in a filter and extracted. Clean filters were similarly extracted as blanks. Extracts were then filtered and reduced in volume to 10.0 ml using a rotary evaporator. The extracts were stored in a freezer at -25°C .

Weights of extracts were determined by evaporating duplicate 100 μl aliquots on a slide warmer at 40°C and weighing the residue on a Cahn Electrobalance. All weights were blank corrected. Samples were protected from light at all times and the work was done in laboratories equipped with yellow lights.

Prior to analysis, an aliquot (4.0 or 5.0 ml) from each sample was pipetted into a pre-rinsed 8 ml amber vial. On the day of analysis, the extract was then evaporated under nitrogen just to dryness. Two hundred-fifty microliters of HPLC grade acetonitrile was pipetted into the vial which was then briefly sonicated.

D.2 PAH Analyses

The cyclohexane fractions were analyzed for polycyclic aromatic hydrocarbons by high performance liquid chromatography (HPLC) on a 0.46 x 25 cm Vydac 201TP54 column (The Separations Group, Hesperia, CA). A 20 μ l aliquot of the concentrated extract in acetonitrile was injected into a reversed phase HPLC system. Solvent composition was linearly programmed from 50% to 100% acetonitrile/ H_2O for 10 minutes and held at 100% acetonitrile for 20 minutes. Flow was 1.0 ml/min. Two absorbance detectors (365 and 340 nm) and a fluorescence detector (360 nm excitation, 440 nm emission) were used for monitoring and quantitation. Fluoranthene, pyrene, chrysene, benzo(e)pyrene and benzo(k)fluoranthene were quantitated with the 340 nm detector, while benz(a)anthracene, benzo(j)fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene were quantitated with the 365 nm detector; perylene concentrations were determined with the fluorescence detector (Table D-1). Quantitation of PAH concentrations employed standard curves of either area or peak height versus ng injected.

Standard PAH mixtures were used to prepare calibration curves as well as to monitor HPLC operation and column condition. A 1:4 dilution of National Bureau of Standards Priority Pollutant PAH's SRM 1647 was used for calibration for most compounds. Two other standards were prepared to include an additional three compounds. A standard containing benzo(e)pyrene and perylene and one containing benzo(j)fluoranthene were prepared in HPLC grade acetonitrile as 1:4 dilutions of stock solutions. These standards were run separately since benzo(b)fluoranthene and perylene were co-eluters as were benzo(e)pyrene and benzo(j)fluoranthene. Figure D-1 is an HPLC

Table D-1. Wavelength Used for Quantitation

<u>Compound</u>	<u>nm</u>
Fluoranthene	340
Pyrene	340
Benz(a)anthracene	365
Chrysene	340
Benzo(j)fluoranthene	365
Benzo(e)pyrene	340, simultaneous equations
Benzo(b)fluoranthene	365
Perylene	fluorescence
Benzo(k)fluoranthene	340
Benzo(a)pyrene	365
Benzo(ghi)perylene	365
Indeno(1,2,3-cd)pyrene	365

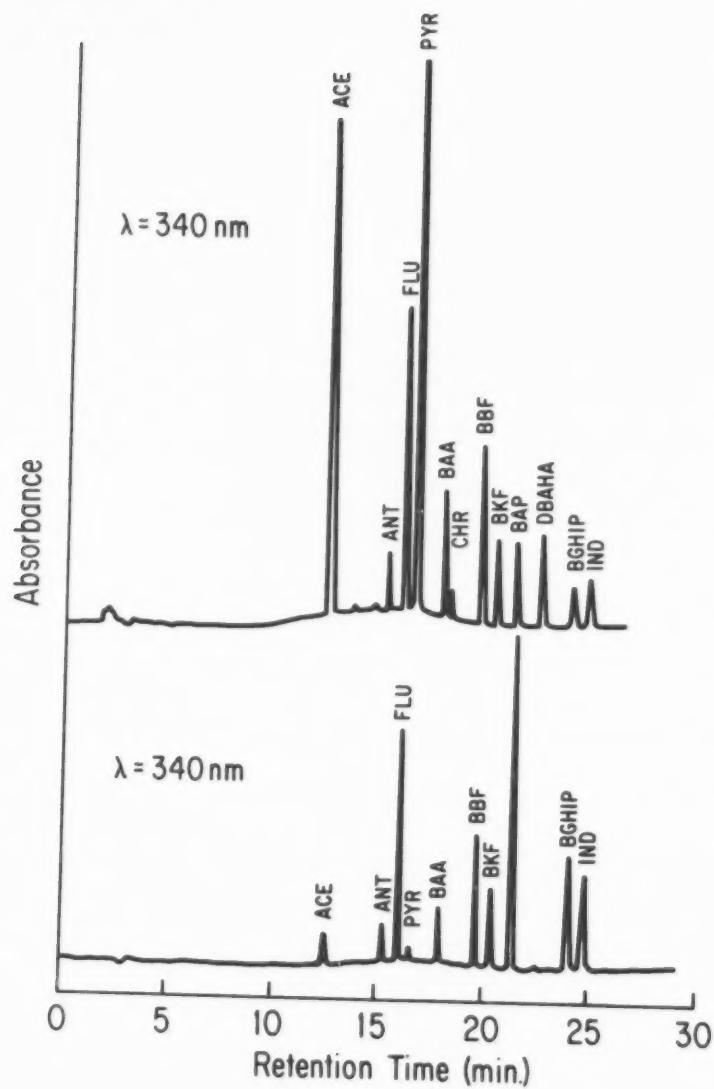


Figure D-1. HPLC Chromatogram of NBS SRM 1647 using the Separations Group Vydac 201TP54 Column.

chromatogram of SRM 1647 at 340 and 365 nm using the Separations Group Vydac column. Figure D-2 shows a chromatogram typical of the New York City samples for the same column.

Calibration curves were prepared for each compound at either 340 or 365 nm. A Spectra Physics 4000 Central Processor was programmed to integrate peak areas using a floating baseline. Plots were constructed for both area and peak height versus concentration (ng injected). Each curve consisted of five concentrations with at least two runs per data point. Correlation coefficients were greater than 0.97. These standard curves were used to calculate the ng per 20 μ l injection for each PAH compound in the actual samples.

Each ambient sample was run at least two times. Individual PAH's were identified by relative retention times and, for compounds detectable at both wavelengths, peak height ratios. Peak height ratios were determined for at least one sample per day. If the 365/340 ratio of a compound was not within 25% of the standard, it was not considered to have been identified (i.e., dibenz(a,h)anthracene).

SRM 1647 was run approximately once every 15 runs to verify that the detectors and integrator were functioning properly. Concentrations were generally within 25% of NBS certified values (usually much better). The PAH standard was also used to monitor column condition. Deterioration of our column, defined as a loss of resolution, was clearly seen with the

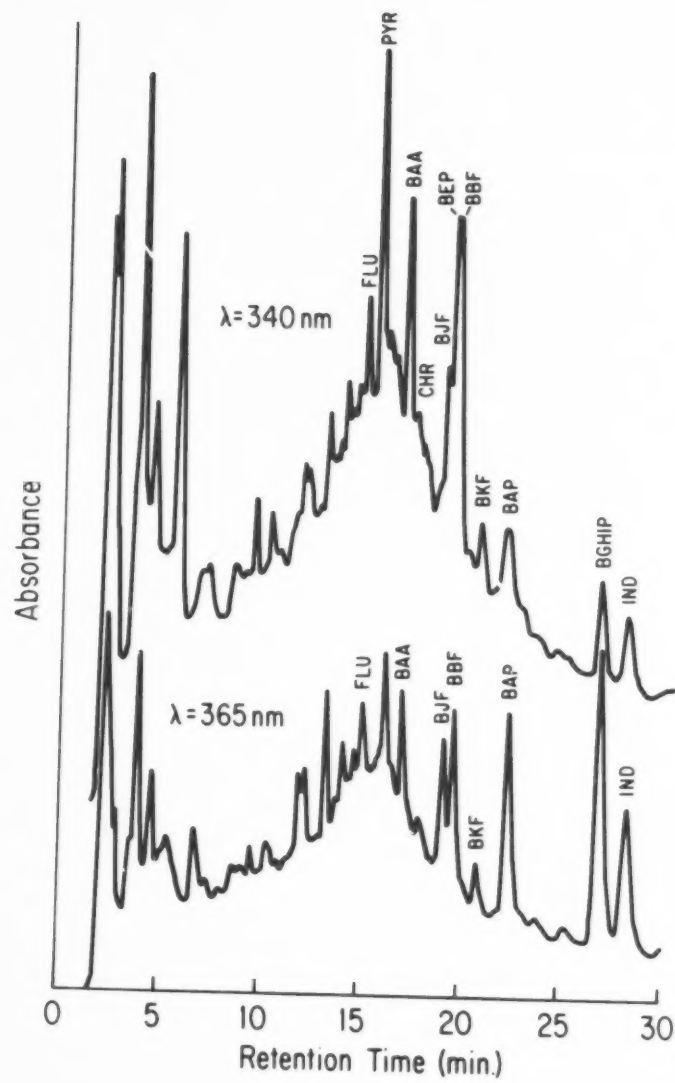


Figure D-2. HPLC Chromatogram of PAH in Cyclohexane Extract of New York City, Oct. 31-Nov. 7, 1979 Sample.

chromatograms of the standard. When this stage was reached, and cleaning the column was no longer effective, it was replaced with a new, identical column.

D.3 Quality Assurance Results

National Bureau of Standards Urban Dust/Organics Standard Reference Material (SRM) 1649 was used as a positive control to 1) determine the reproducibility of our extraction technique, and 2) ascertain the suitability of a floating baseline integration and/or peak height measurement in determining concentrations of certified and noncertified PAH's. Two hundred milligrams of SRM 1649 was placed on each of six pre-fired Gelman AE glass fiber filters; instead of NBS's recommended 1 g sample size, 200 mg was used since ambient samples are closer to this amount. The six loaded filters plus two blanks were extracted by the procedure previously discussed. The results of duplicate mass determinations following sequential Soxhlet extractions are shown in Table D-2. Relative standard deviations were 2.0, 7.0 and 10.0% for the cyclohexane-, dichloromethane- and acetone-soluble fractions, respectively. The results are quite reproducible and consistent with previous experiments in this laboratory in which duplicate samples of airborne particulate matter collected on filters were sequentially extracted.

The results of the analyses of 4 of the samples of NBS SRM No. 1649 for PAH are summarized and compared to the values reported by NBS in Table D-3. Values for individual samples are reported in Table D-4. Samples No. 1 and No. 6 were used for method development and to determine integrator settings and satisfactory chromatograms at $\lambda = 365 \text{ nm}$ were not available. The averages reported in Table D-3 are therefore only for samples 2 through 5 for which

Table D-2. Summary of Results of Replicate Extractions of
NBS Standard Reference Material 1649

Sample No.	Concentration (mg extract per g. of particles)		
	CX ^a .	DCM ^a .	ACE ^a .
1	27.2	13.1	37.0
2	27.8	14.5	38.0
3	26.9	15.7	-
4	28.2	14.1	30.4
5	26.7	15.9	36.3
6	28.1	14.6	31.7
$\bar{X} \pm \text{SD}$	27.5 ± 0.6	14.6 ± 1.0	34.7 ± 3.4

a. CX = Cyclohexane-soluble organics; DCM = dichloromethane-soluble organics; ACE = acetone-soluble organics.

Table D-3. Comparison with NBS Values for SRM No. 1649

Compound ^a Number of Samples	µg PAH per g. NBS Particles			
	NYU Values	NBS Values (by method)		
	Mean±S.D. (%RSD) 4	GC 4	LC-I 18	LC-II 9
Fluor	6.6 ±0.2 (3)	7.3 ±0.2	7.0 ±0.5	6.8 ±0.4
Pyr	4.8 ±0.1 (2)	7.2 ±0.2	6.3 ±0.4	6.2 ±0.2
BaA	2.5 ±0.4 (16)	2.4 ±0.1	2.8 ±0.3	2.4 ±0.1
Chry	2.4 ±1.1 (46)	nd	3.5 ±0.1	3.7 ±0.2
BjF	3.0 ±0.8 (27)	nd	nd	nd
BeP	2.7 ±1.0 (37)	3.3 ±0.2	nd	nd
BbF	4.9 ±0.8 (16)	6.2 ±0.3	nd	nd
Per	0.62±0.02(3)	0.84±0.09	0.80±0.04	0.65±0.02
BkF	1.3 ±0.4 (31)	nd	2.0 ±0.1	1.2 ±0.1
BaP	3.1 ±0.3 (10)	3.0 ±0.3	2.6 ±0.4	2.6 ±0.1
DBahA	0.33±0.07(21)	nd	nd	0.41±0.07
BghiP	4.0 ±0.5 (13)	4.7 ±0.2	3.9 ±0.8	5.2 ±0.6
IndP	2.9 10.4 (14)	3.3 ±0.3	3.4 ±0.4	3.6 ±0.2

nd = not determined.

a. Fluor = Fluoranthene, Pyr = Pyrene, BaA = Benz(a)anthracene, Chry = Chrysene, BjF = Benzo(j)fluoranthene, BeP = Benzo(e)pyrene, BbF = Benzo(b)fluoranthene, Per = Perylene, BkF = Benzo(k)fluoranthene, BaP = Benzo(a)pyrene, DBahA = Dibenz(a,h)anthracene, BghiP = Benzo(ghi)perylene, IndP = Indeno(1,2,3-cd)pyrene,

Table D-4. Concentrations of PAH Determined for Individual Samples

Compound ^a	$\mu\text{g PAH/g. NBS SRM \# 1649}$						Mean $\pm$ S.D.	
	Sample #							
	1	2	3	4	5	6	n=4	n=6
Fluor	8.35	6.85	6.68	6.40	6.60	7.85	6.6 $\pm$ 0.2	7.1 $\pm$ 0.8
Pyr	6.51	4.70	4.94	4.63	4.81	5.73	4.8 $\pm$ 0.1	5.2 $\pm$ 0.8
BaA	- ^b	2.16	2.32	2.51	3.04	-	2.5 $\pm$ 0.4	-
Chry	3.76	1.00	3.63	2.31	2.49	3.43	2.4 $\pm$ 1.1	2.8 $\pm$ 1.1
BjF	-	3.85	2.11	2.41	3.42	-	3.0 $\pm$ 0.8	-
BeP	-	3.64	1.32	3.34	2.47	-	2.7 $\pm$ 1.0	-
BbF	-	4.12	4.56	5.24	5.82	-	4.9 $\pm$ 0.8	-
Per	0.87	0.64	0.62	0.60	0.60	0.77	0.62 $\pm$ 0.02	0.68 $\pm$ 0.11
BkF	2.02	1.59	1.59	1.29	0.75	1.17	1.3 $\pm$ 0.4	1.4 $\pm$ 0.4
BaP	-	1.97	3.35	2.65	3.27	-	3.1 $\pm$ 0.3	-
DBahA	0.42	0.42	0.35	0.25	0.29	0.35	0.33 $\pm$ 0.07	0.35 $\pm$ 0.07
BghiP	-	3.69	3.54	3.98	4.64	-	4.0 $\pm$ 0.5	-
IndP	-	2.34	2.76	2.91	3.43	-	2.9 $\pm$ 0.4	-

a. See Table D-3.

b. - = chromatogram for $\lambda = 365$ nm not available.

complete sets of measurements were available. The concentrations determined for the PAH in the SRM No. 1649 are generally in good agreement with values reported by NBS. The values for pyrene and chrysene are about 30% lower than the NBS values. This is probably due to volatilization losses during solvent evaporation. The concentrations determined for benzo(b)fluoranthene and benzo(k)fluoranthene are also somewhat lower than the values reported by NBS. A composite sample of the dichloromethane (DCM) extracts of the NBS samples was analyzed for PAH to determine if incomplete extraction by cyclohexane and carry-over into the next fraction might account for somewhat lower values since the NBS analytical methods employed either a benzene-methanol mixture or dichloromethane for extraction. Traces of benzo(b)- and benzo(j)fluoranthene were observed in the DCM extracts; for the benzo(b)- isomer, approximately 5% of the total reported by NBS could be accounted for in this way. Other sources of uncertainty include the smaller sample size used and the uncertainties in baseline.

APPENDIX E

Receptor Source Apportionment Models for Two Polycyclic Aromatic Hydrocarbons

Published in:

Proceedings, Receptor Models Applied to Contemporary Pollution Problems, APCA Specialty Conference, SP-48, S. Dattner and P. Hopke, Technical Editors, Air Pollution Control Association, 1982.

RECEPTOR SOURCE APPORTIONMENT MODELS FOR TWO
POLYCYCLIC AROMATIC HYDROCARBONS

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The feasibility of developing receptor models for polycyclic aromatic hydrocarbons (PAH) has been investigated using benzo(a)pyrene (BAP) and chrysene (CHR) as prototype compounds. Factor analysis was used to identify elemental source tracers and then a multiple linear regression equation was developed to relate concentrations of individual PAH to Pb and V, tracers for traffic-related and oil combustion emissions in New York City. Statistically significant equations were obtained for both compounds, despite the somewhat limited number of cases available for modeling. Oil-burning accounted for $114 \pm 22\%$ of airborne BAP during the heating season; $62 \pm 27\%$ of airborne particulate chrysene was traffic-related while $19 \pm 22\%$ was related to oil-burning. The multiple regression coefficient for Pb in the CHR model was in good agreement with the estimated ratio of CHR/Pb in airborne particles sampled in tunnels. Further validation of the models was not possible due to the lack of appropriate source emissions measurements.

RECEPTOR SOURCE APPORTIONMENT MODELS FOR TWO POLYCYCLIC AROMATIC HYDROCARBONS

Introduction

The polycyclic aromatic hydrocarbon (PAH) fraction of airborne particles is the most carcinogenic in animal bioassays and is, therefore, of major interest from the standpoint of environmental health¹. Many of the PAH, including benzo(a)pyrene and chrysene, have been classified by the EPA as priority pollutants. Although these compounds are known to originate from the combustion of carbonaceous matter such as oil, coal or refuse, methods to determine the relative contributions of various types of combustion sources at a given location have not been developed. In principle, it should be possible to identify major contributing sources and to estimate their contributions at a given location using receptor source apportionment modeling techniques. In practice, limited source composition data, volatilization of lower molecular weight compounds during sampling and atmospheric reactions occurring between source and receptor may hinder the development of these types of receptor models.

A preliminary investigation was undertaken to determine the feasibility of developing receptor models for PAH compounds and to identify some of the problems which might arise in model development. The FA/MRRM (factor analysis/multiple regression receptor model) approach developed by Kneip, Kleinman and co-workers²⁻⁴ was used in the present analysis. Factor analysis was used to identify independent source tracers and then a multiple regression equation was developed relating the concentrations of the individual PAH to the source tracers. This approach was selected because of the limited source composition data for trace metals and PAH determined simultaneously. In addition, changes which may occur between the source and the receptor are automatically incorporated into the coefficients of the source tracers with the method.

Two compounds were selected for model development. Benzo(a)pyrene (BAP) was selected because it has been widely used as an index of the PAH fraction and it is concentrated in the particulate phase ($> 90\%$)^{5, 6}. Chrysene (CHR) was selected because it is distributed between the gaseous and particulate phases and the distribution changes with temperature⁶; thus, it presents a more complex problem for source apportionment via receptor modeling.

Experimental

Weekly samples of total (TSP) and respirable ($\leq 3.5 \mu\text{m}$, A.D.) (RSP) suspended particulate matter were collected at the New York University Medical Center Roof Station, which is located on the east side of Manhattan and has been described⁷ in a previous report. The RSP samples were collected on pre-ignited filters (Gelman AE) from August 1, 1978 to August 30, 1979. Half of each RSP sample was extracted sequentially with cyclohexane, dichloromethane and acetone, respectively, as described previously⁷. Samples were stored at -35°C prior to extraction, but were extracted within a few days of collection. Samples were protected from light at all times. Extracts were stored in a freezer until PAH analysis. The cyclohexane extracts were analyzed for PAH by a thin-layer/gas chromatographic method⁸. Concentrations of BAP were below the limit of detection (0.1 ng/m^3) from 8/1-9/28/78 and from 4/11-8/30/79, leaving for this compound data only associated with the heating season.

A portion of each RSP and TSP sample was analyzed for selected trace metals: Pb, V, Cu and Mn. These metals had been previously identified as source tracers for major sources in New York City^{3, 4}. Portions of the TSP and a second RSP sample, collected on Spectrograde filters, were analyzed for water-soluble sulfate^{3, 4}. Daily values of the 7 A.M. mixing height and windspeed aloft, measured at Fort Totten, N.Y., were obtained from the National Weather Service. Weekly averages were computed for use in the modeling. Weekly averages of daily average temperature measures in Central Park (in Manhattan) were also calculated.

The Statistical Package for the Social Sciences (SPSS), version 8⁹, 10 was used for statistical analyses and model development. Listwise deletion of missing data was employed so that the analyses were based only on cases which included a complete set of data for all variables. Factor analysis (principal factoring, R-type, with Varimax rotation) had been used previously on this data set to identify source types of tracers⁷. In general, V, Pb, SO₄²⁻ and Cu were found on separate factors. Manganese in the RSP was associated with Pb. This appeared to be due to the use of methylcyclopentadienyl tricarbonyl as an octane booster in gasoline during this period¹¹.

Stepwise multiple linear regression models were then developed. These were of the form:

$$[\text{PAH}] = k_1 T_1 + k_2 T_2 + \dots + k_i T_i + R \quad (1)$$

where $[\text{PAH}]$ is the ambient concentration of the PAH species of interest, T_i = the ambient concentration of the source tracer, k_i = the regression coefficient of source tracer, T_i , R = the residual, i.e., the concentration of PAH not associated with the modeled sources. Respirable Pb and V, tracers for traffic-related and oil-burning sources, respectively^{3, 4}, were used in the models since these elements were most highly correlated with CHR and BAP.

The constants k_i relate source emissions to ambient concentrations according to the equation:

$$k_i = \frac{\alpha_{ij} [\text{PAH}]_j}{T_j} \quad (2)$$

where $[\text{PAH}]_j$ = the concentration of PAH in emissions from source j , T_j = the concentration of the tracer element in emissions from source j , and α_{ij} = the coefficient of fractionation which describes changes in the ratio $[\text{PAH}]_j/T_j$ which may occur between the source and receptor as a result of physical and chemical processes.

All ambient concentrations of PAH and source tracers were normalized to constant dispersion conditions¹² using the dispersion factor proposed by Holzworth¹³, e.g.,

$$[\text{PAH}]_N = \frac{[\text{PAH}] \text{ h} \cdot \text{s}}{4200 \text{ m}^2/\text{sec}} \quad (3)$$

where $[PAH]_N$ is the dispersion normalized concentration, h is the 7 A.M. mixing height, s is windspeed aloft and $4200 \text{ m}^2/\text{sec}$ is an average product of $h \cdot s$ for New York City. This technique has been used previously⁷.

The distributions of the ambient concentrations of both BAP and CHR were examined prior to the regression analyses. These are shown in Figure 1. The 22 values of BAP were approximately normally distributed, but the CHR appeared to follow a bimodal distribution. The lower concentrations were generally associated with the summer months. This suggested that shifts in the vapor-particle distribution might be the source of the bimodal distribution. Vapor phase concentrations of CHR were then estimated using the equation of Yamasaki, *et al.*⁶, which is based on the Langmuir model for a vapor adsorbed on a solid;

$$\log (CHR)_V = \frac{-5826}{T} + 24.89 + \log \frac{(CHR)_P}{(TSP)} \quad (4)$$

where $(CHR)_V$ and $(CHR)_P$ are the concentrations of CHR in the vapor and particle phases, respectively, T is temperature in degrees Kelvin and TSP is the concentration of total suspended particulate matter. The distribution of the concentrations of total CHR (vapor + particle) is shown in Figure 2 and the data are obviously more normally distributed than the original particle phase concentrations. A source apportionment model for total chrysene $(CHR)_T$ was also developed.

Results

The results of the regression analyses are summarized in Table I. All three equations were statistically significant at the $p < 0.02$ level. The values of R^2 were relatively low compared to models of this type developed for other variables^{2-4, 7}, but fewer data were available for the PAH compound models, particularly for BAP. The reduced set of data for the BAP was inadequate to obtain a coefficient for Pb. Comparing the models for CHR_P and CHR_T , the coefficients for Pb did not differ significantly between the two models but the standard error of the Pb coefficient was greater for the CHR_T model. The coefficients of V did differ slightly, but were not statistically different. This and the greater residual for the CHR_T model presumably are associated with the additional uncertainties introduced into the data from the calculated vapor concentrations.

Discussion

The average source contributions calculated from the models are presented in Table II. For BAP, the oil-burning sources in New York City during this winter period accounted for $114 \pm 22\%$ of the total concentration. Based on the model, traffic-related sources contributed, at most, only a few percent of the BAP. This is consistent with the reduced BAP emissions associated with catalyst equipped cars¹⁴ and the location of the sampling site on the roof of a 15 story building.

Traffic-related sources accounted for 1.42 and 1.65 ng/m³ of the particulate and total chrysene concentrations while oil-burning was a lesser contributor. The model for particulate chrysene accounted for about 80% of the chrysene. The model based on the more normally distributed data for the total chrysene accounted for only 58% of the total. Although, in principal, this is a more physically appropriate model, the uncertainties in the calculated vapor concentrations led to a less satisfactory model in terms of both R² and the residual CHR. It should be noted, however, that the equation used to calculate vapor phase concentrations was determined for TSP rather than RSP samples and was based on measurements made in a different city.

In Table III, the average percent deviation of the concentration predicted by each of the particulate models from the actual is presented as a function of concentration. The greatest deviations were observed for low concentrations, which are associated with the greatest analytical uncertainties. The relative deviations between actual and predicted concentrations for these compounds, in general, are of the same order of magnitude as those observed for many trace elements in receptor models¹⁵.

In relationship between the coefficients of the models and the ratios of BAP and CHR to the source tracer in source emissions, can provide evidence of the validity of the developed models, as shown in eqn. (2). However, in only a few instances have both PAH and trace element compositions been measured simultaneously. Kebbekus and co-workers¹⁶ recently measured the concentrations of certain PAH compounds and of Pb for 4 samples collected in the Lincoln Tunnel (between Weehawken, N.J. and Manhattan). The ratio of BAP/Pb averaged 0.00145 ± 0.0056 ; chrysene was not determined. This ratio cannot be compared directly to the models, since there were insufficient data to fit the Pb coefficient in the BAP model. Grimmer and co-workers¹⁷ reported concentrations of PAH for 4 samples collected in a tunnel with car traffic in Essen, Germany. The BAP/CHR ratio was 0.65 ± 0.14 . If the data for the two tunnels are combined, the CHR/Pb ratio can be estimated as 0.0022, which is in very good agreement with the Pb coefficient of the model for particulate chrysene.

Grimmer and co-workers¹⁷ have also determined concentrations of PAH in an area of Essen dominated by oil-burning. The ratio of BAP/CHR for the area was 0.3. The oil-burning contributions for New York City during the winter months can be calculated from the models as 1.61 ± 0.35 and 0.63 ± 0.72 ng/m³, respectively, for BAP and CHR, giving a BAP/CHR ratio of 2.6 ± 1.2 . The agreement in this instance is poor; however, the differences in types of oil (No. 2 vs. No. 4 and No. 6) and oil-burning equipment may affect such ratios. Ideally, comparisons should be with source emission measurements made in New York City.

Conclusions

This preliminary study has demonstrated the feasibility of developing FA/MR models for PAH compounds. The Pb coefficient of the CHR model is in quite good agreement with available source emission data and supports the validity of the CHR model. The poor agreement between actual and predicted concentrations at low PAH concentrations suggests a need for improved analytical methods. Corrections for shifts in the vapor-particle distribution of CHR due to seasonal temperature variations have been found to give an approximately normal distribution for concentrations of total CHR, although these corrections did not give any improvement in the model.

The greatest need for the development of such models is the need for appropriate source emissions composition data. Source emission samples must be collected at close to ambient conditions, i.e., temperature and dilution, in order to insure that vapors have condensed and adsorbed on the particles. Source samples should be analyzed for trace elements as well as PAH compounds. Since much more is known about the sources and stability of the trace elements, these species can be very useful for model development and verification.

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References

1. D. Hoffmann and E. L. Wynder, "Organic particulate pollutants - chemical analyses and bioassays for carcinogenicity," In *Air Pollution*, A. C. Stern, Ed., 3rd ed., 2: pp 361-455, Academic Press, Inc., New York, N.Y. 1977.
2. T. J. Kneip, M. T. Kleinman and M. Eisenbud, "Relative contribution of emission sources to the total airborne particulates in New York City," Proceedings of the Third IUAPPA International Clean Air Congress, Dusseldorf, Germany, pp C96-C97 (1973).
3. M. T. Kleinman, B. S. Pasternack, M. Eisenbud and T. J. Kneip, "Identifying and estimating the relative importance of sources of airborne particulates," *Environ. Sci. & Technol.*, 14: 62-65 (1980).
4. T. J. Kneip, R. P. Mallon and M. T. Kleinman, "Multiple regression models for source apportionment," *Atmos. Environ.*, In Press.
5. W. Cautreels and K. VanCauwenberghe, "Experiments on the distribution of organic pollutants between airborne particulate matter and the corresponding gas phase," *Atmos. Environ.*, 12: 1133-1141 (1978).
6. H. Yamasaki, K. Kuwata and H. Miyamoto, "Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons," *Environ. Sci. & Technol.*, 16: 189-194 (1982).
7. J. M. Daisey and T. J. Kneip, "Atmospheric particulate organic matter: Multivariate models for identifying sources and estimating their contributions to the ambient aerosol," In *Atmospheric Aerosol: Source/Air Quality Relationships*, E. S. Mascias and P. K. Hopke, Eds., ACS Symposium Series No. 167, pp 197-221, American Chemical Society, Washington, D.C. (1981).
8. J. M. Daisey and M. A. Leyko, "Thin-layer gas chromatographic method for the determination of polycyclic aromatic and aliphatic hydrocarbons in airborne particulate matter," *Anal. Chem.*, 51: 24-26 (1979).
9. N. H. Nie, C. H. Hull, J. G. Jenkins, K. Steinbrenner and D. H. Bent, *SPSS Statistical Package for the Social Sciences*, 2nd ed., McGraw-Hill Book Co., New York, N.Y. (1975).

10. C. H. Hull and N. H. Nie, Eds., SPSS Update, New Procedures and Facilities for Releases 7 and 8, McGraw-Hill Book Co., New York, N.Y. (1979).
11. P. J. Liroy, R. P. Mallon and T. J. Kneip, "Long-term trends in total suspended particulates, vanadium, manganese, and lead at near street level and elevated sites in New York City," J. Air Pollut. Control Assoc., 30: 153-156 (1980).
12. M. T. Kleinman, T. J. Kneip and M. Eisenbud, "Seasonal patterns of airborne particulate concentrations in New York City," Atmos. Environ., 10: 9-11 (1976).
13. G. C. Holzworth, "Mixing depths, wind speeds and air pollution potential for selected localities in the U.S.," J. Appl. Meteorol., 6: 1039 (1967).
14. R. L. Williams and S. J. Swarin, "Benzo(a)pyrene emissions from gasoline and diesel automobiles," SAE Technical Paper No. 790419, Society of Automotive Engineers, Inc., Warrendale, PA 15096 (1979).
15. D. J. Alpert and P. K. Hopke, "A determination of the sources of airborne particles collected during the Regional Air Pollution Study," Atmos. Environ., 15: 675-687 (1982).
16. B. Kebbekus, et al., New Jersey Institute of Technology, Newark, N.J. Personal Communication.
17. G. Grimmer, K.-W. Naujack and D. Schneider, "Changes in PAH-profiles in different areas of a city during the years," In Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects, Fourth International Symposium, A. Bjorseth and A. J. Dennis, Eds., pp 107-125, Batelle Press, Columbus, Ohio (1980).

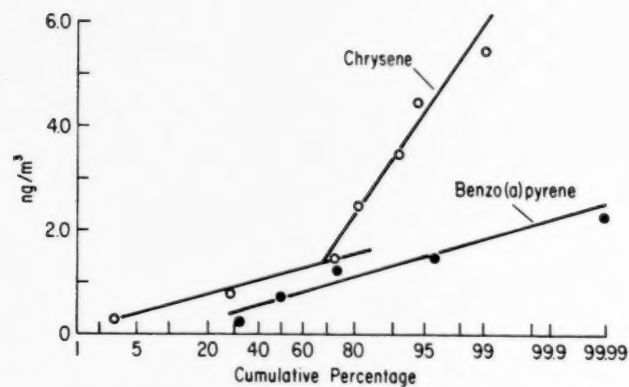


Figure E-1. Distributions of particulate benzo(a)pyrene and chrysene ambient concentrations

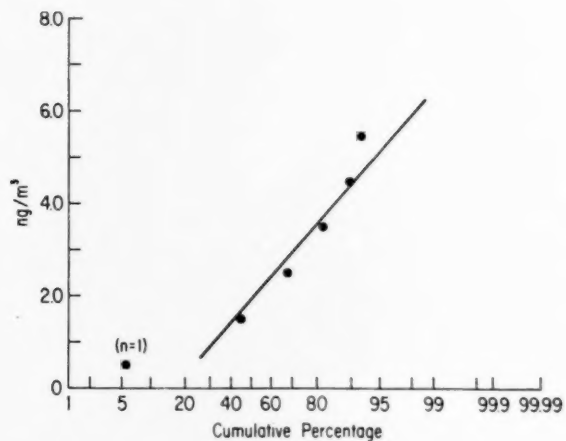


Figure E-2. Distribution of total chrysene (particle + vapor) concentration.

Table E-1. STEPWISE LINEAR REGRESSION MODELS FOR BAP AND CHR

Dependent Variable	n ^a	Coefficients of Source Tracers $\pm$ S.E.		Residual	R ²	F	P
		PB	V				
BAP	22	-	0.017 $\pm$ 0.003	-0.23 $\pm$ 0.41	0.31	4.4	0.02
CHR _P	39	0.0016 $\pm$ 0.0007	0.0059 $\pm$ 0.0068	0.43 $\pm$ 0.45	0.41	12.5	<0.001
CHR _T	35	0.0017 $\pm$ 0.0010	0.0025 $\pm$ 0.0106	1.38 $\pm$ 0.62	0.27	6.15	0.005

a. n - number of cases.

TABLE II. AVERAGE SOURCE CONTRIBUTIONS CALCULATED FROM REGRESSION MODELS

PAH	Sampling Period	Source Contributions, ng/m ³		
		Traffic-related	Oil-Burning	Residual
BAP	10/12/78-4/11/79	-	1.84 $\pm$ 0.36 (114 $\pm$ 22%)	-0.23 $\pm$ 0.41 (-14 $\pm$ 25%)
CHR _P	8/ 1/78-8/30/79	1.42 $\pm$ 0.62 (63 $\pm$ 27%)	0.43 $\pm$ 0.49 (19 $\pm$ 22%)	0.42 $\pm$ 0.45 (19 $\pm$ 20%)
CHR _T	8/ 1/78-8/30/79	1.65 $\pm$ 0.97 (51 $\pm$ 30%)	0.18 $\pm$ 0.77 (6 $\pm$ 24%)	1.38 $\pm$ 0.62 (43 $\pm$ 19%)

TABLE III. PERCENT DEVIATION OF PREDICTED FROM ACTUAL VALUE AS A FUNCTION OF CONCENTRATION

Dispersion Normalized Concentration (ng/m ³)	Average % Deviation of BAP ^a (n) ^b	Average % Deviation of CHR _P (n) ^b
0 -0.49	81 (6)	198 (7)
0.5-0.99	82 (5)	81 (6)
1.0-1.99	54 (2)	83 (7)
2.0-2.99	31 (6)	32 (7)
3.0-3.99	22 (3)	38 (3)
4.0-4.99	-	30 (6)
>5.0	-	53 (3)

a. 100% $\times$ (actual - predicted)/actual.

b. n - number of cases.

APPENDIX F
QUALITY ASSURANCE PLAN

A comprehensive program of quality assurance is essential in any research program, but particularly so when large numbers of data are generated. The quality assurance program for this investigation, as for other ongoing investigations in this laboratory, includes a number of elements to assure maximum accuracy and precision for the generated data.

1. Laboratory Management and Personnel - The laboratory management system is responsible for establishing and implementing quality assurance programs. Both laboratory organization, competent professional staff and good communications are key elements in implementation of quality assurance programs. An organizational chart for this investigation, with special emphasis on quality assurance aspects, is presented in Figure F-1.

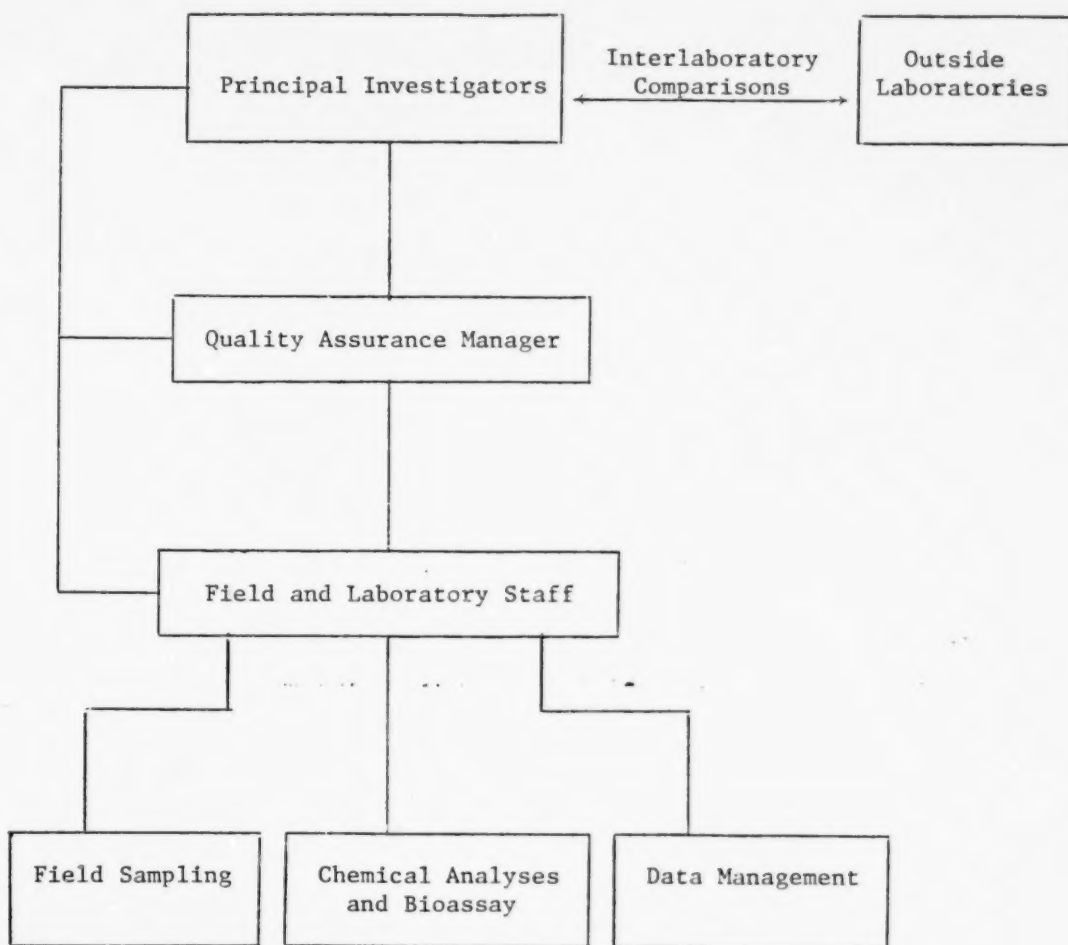
The quality assurance program is formally reviewed by all NYU staff on an annual basis. Data from the quality assurance program are reviewed quarterly to provide ongoing reviews of various aspects of the quality assurance program.

2. A manual of Standard Methods in use in our laboratory was prepared in 1979. This manual is updated when new methods are developed or when old methods are modified.

3. Sampling - Sampling sites are chosen, in so far as possible, so that the samples will be representative of a variety of sources in each of the urban areas to be investigated. Each site is examined by the Principal Investigators prior to initiation of sampling.

Protocols for sample preparation, sampling in the field, for transport and storage of samples and for record keeping are reviewed with

Figure F-1. Organization and Management of Quality Assurance Program



technical and field personnel prior to each sampling campaign. Particle samplers are calibrated in the field immediately before and after each sampling campaign.

4. Analytical Measurements -

- a. Analytical instrumentation - All analytical instruments are routinely maintained under service contracts and regularly calibrated. Records of use and maintenance are kept for each instrument.
- b. Chemical analysis - The quality assurance practices for chemical analysis in our laboratories include:
 - 1) use of high purity chemical reagents;
 - 2) routine analysis of blanks (or negative controls);
 - 3) routine preparation and use of calibration standards and curves, NBS Standard No. 1647, Priority Pollutant Polynuclear Aromatic Hydrocarbons in Acetonitrile is used daily for calibration of the High Pressure Liquid Chromatograph;
 - 4) analysis of NBS standards - spiked filters and fly ash - for trace metal analysis (positive controls); NBS Standard Reference material 1649, Urban Dust and Organics will be used as a positive control for determination of extractable organic mass fractions and for PAH analyses of the Philadelphia samples
 - 5) interlaboratory comparisons - The laboratory participates in interlaboratory comparisons on analytical methods as frequently as possible;
 - 6) review of methods, organization, record keeping and results of analysis.

5. Record Keeping -

a. Records kept routinely are:

- 1) all samples received;
- 2) all analyses;
- 3) analyses of blanks, standards and reference materials;
- 4) instrument maintenance, use and calibrations; and
- 5) computer data files.

b. All ambient measurement data are eventually stored in a permanent computer file. In addition, a central reference notebook is maintained as a guide to the records available on each type of analysis and their location.

c. Data transmission - Analytical data are transmitted to the project's computer manager for incorporation into the permanent computer file. Computer print outs are then validated against original records prior to statistical analysis.